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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments and chemical engineering problems relating to rubber or its allied substances.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

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Minutes of Recent Meetings

Boston Group Meeting

A joint meeting of the Northeastern Section of the American Chemical Society and the Boston Rubber Group was held at the University Club, Boston, January 12.

Papers were delivered at the afternoon session, a dinner followed, and the program was completed at an evening session with the presentation of more papers. The papers which were presented included the following five: A. A. Somerville (R. T. Vanderbilt & Co.), "Some New Laboratory Work on Rubber Compounding;" T. M. Knowland (Hood Rubber Company), "Tire Design with Relation to Comfort, Flexibility, and Wear;" W. B. Wiegand (Binney & Smith Co.), "Reduction of Rubber Stress Strain Determinations;" E. R. Bridgwater (E. I. du Pont de Nemours & Co.), "Antisofteners and Fatigue Inhibition;" Sidney N. Cadwell (United States Rubber Co.), "Antioxidants."

Financial Statement

Received from Arnold H. Smith, former Secretary-Treasurer, October 18, 1927	$298.86	
Money received (dues and subscriptions)	1,607.98	$1,906.84
Disbursements:		
Printing, stationery, etc.	$135.51	
Postage	27.98	
Stenographic services	79.01	
Telegrams	5.28	
Refunds	4.00	
Reprints from *The Rubber Age*	226.55	
C. C. Davis (Misc. Expense)	47.25	
Translation	45.00	
Mack Printing Company (postage, insurance, mailing lists, printing Vol. I, No. 3)	334.34	904.92
Balance on hand December 20, 1928		$1,001.92

H. E. SIMMONS, *Secretary-Treasurer*

Financial Statement—(*Continued*)

Cost of Publishing the First Four Numbers, April, July, October and November, Vol. I, 1928, *Rubber Chemistry and Technology*

(Contributed by the Rubber Association of America)

Reprinting from *Industrial and Engineering Chemistry:*		
For the April Number	$654.76	
For the July Number	962.54	$1,617.30
Summary from the above Financial Statement of the Rubber Division:		
Reprinting from *The Rubber Age*	$226.55	
Editor's miscellaneous expenses	47.25	
Translation	45.00	
Mack Printing Co. for October Number	334.34	
Mack Printing Co. for November Number	249.91*	$903.05
Total		$2,520.35

HARRY L. FISHER, *Associate Editor*

* Not included in the Secretary's statement.

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the October 10 and 20, and November 10 and 20, 1928, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial and trade journals throughout the world.

The preparation and use of rubber solutions. K. GASTEN. *Chem.-tech. Ind.* **29**, 193–4, 209–10(1928).—A review and description of rubber cements used for shoes and other important products. C. C. DAVIS

Cooling water for use in rubber manufacturing plants. W. F. SCHAPHORST. *Rubber Age* (N. Y.) **23**, 431–2(1928). C. C. DAVIS

Technical rules for the formulation of rubber mixtures. WERNER ESCH. *Kunststoffe* **18**, 53–5, 86–90, 107–13(1928).—See *C. A.* **22**, 511. C. C. DAVIS

Power consumption of calenders. J. MORRISON. *Trans. Inst. Rubber Industry* **3**, 480–87(1928). C. C. DAVIS

Artificial silk and its uses in the rubber trade and possible lines of development. A. B. SHEARER. *Trans. Inst. Rubber Industry* **3**, 454–61(1928). C. C. DAVIS

Further studies of rubber under compression. C. H. BIRKITT AND T. J. DRAKELEY. *Trans. Inst. Rubber Industry* **3**, 462–7(1928).—In continuation of earlier expts. (cf. *C. A.* **20**, 1920), the influence of the area and thickness of the test piece and of the friction between the compression plates and the upper and lower surfaces of the test piece were investigated. The compression is proportional to the original thickness but corrections for area follow no definite law and must be detd. experimentally. The compression at given loads depends upon the lubricant. A general discussion follows. C. C. DAVIS

Carbon blacks and their use in rubber. I. Comparative properties of blacks and tests in uncured rubber. NORRIS GOODWIN AND C. R. PARK. *Ind. Eng. Chem.* **20**, 621–7(1928).—The phys. and chem. properties of 5 C blacks and of rubber mixts. contg. them were studied to det. the relative value of the individual blacks as pigments in tire treads. The blacks included: (1) "Charlton" lampblack, an oil black; (2) "Micronex," made by the channel process black for rubber; (3) "Super Spectra," made by the channel process for varnishes and enamels; (4) "Thermatomic," made by thermal decompn. of natural gas, and (5) "Goodwin," made by incomplete combustion of natural gas at high temps. The true d., apparent d., particle size and shape, x-ray structure, tinting strength, light scattering and absorption, extractable substances, adsorptive capacity, moisture content, oil absorption capacity, sedimentation max. capacity of incorporation in rubber, the behavior during the milling operation, the soly. of the resulting mixts. in C_6H_6, the plasticity of these mixts. and their tendency to bloom were detd. **II. Experiments in cured rubber.** *Ibid* 706–15.—The 5 C blacks were tested in rubber mixts. with different accelerators to det. the phys. properties of a C black which are most responsible for the properties of rubber mixts. contg. the black. The relative properties of the mixts. were judged by stress-strain data, hardness and resistance to abrasion. The results indicate that particle size, adsorption capacity and the nature of the non-C components all play a part in detg. the phys. properties of a rubber mixt. contg. the C black. Of these the adsorption capacity has the most influence on the properties of rubber mixts. In all but 1 case, the higher the adsorption capacity the more the C black retarded the rate of cure. Resistance to abrasion does not vary directly with tensile strength or resilient energy, but is a complex function of the stress-strain curve and particularly of the hardness. Increased resistances to abrasion with increased proportions of C black indicate that a C black which is inferior to another in the same proportion may in larger proportions excel the other. The effects with stearic acid and with the individual accelerators are described in detail. C. C. DAVIS

Effect of various types of carbon black on certain physical properties of rubber compounds. D. J. BEAVER AND T. P. KELLER. *Ind. Eng. Chem.* **20**, 817–9(1928).—Tests of various C blacks in vulcanized rubber show that in general the presence of O in C black retards the rate of vulcanization in direct proportion to the quantity of O adsorbed by the black, and that O decreases the phys. properties obtainable with a given proportion of an accelerator. Furthermore, aging data show that the presence of O in the black increases the rate of deterioration, though this rate does not increase in direct proportion to the quantity of O. Therefore blacks which contain a relatively low proportion of O, such as "Thermatomic" black and acetylene black, give rubber mixts. with better aging properties than do blacks like lampblack and channel C blacks, which contain relatively large quantities of O. No correlation could be found between the acetone ext., I absorption and oil absorption of the blacks and the effects of the blacks on the rate of vulcanization and on the aging of the rubber mixts. contg. them. C. C. DAVIS

The permeability of rubber and methods of testing it. H. A. DAYNES. *Trans. Inst. Rubber Industry* **3**, 428–53(1928).—A crit. review and discussion of the phenomena of *permeation, absorption, diffusion, equil. conditions,* and the *influence of various factors on permeation, diffusion and the time to reach equil.,* including the nature of the gas, the pressure, the thickness, the temp., the state of vulcanization, and the presence of compounding ingredients. The practical importance of these phenomena in the deterioration of air bags for curing tires, in tennis balls, inner tubes and balloons, in the vapor cure, in the Peachey process, in the natural and artificial aging of rubber, in connection with antioxidants, in rubber under expansion, in drying rubber, and in elec. insulation are then discussed. Finally *methods of measuring the permeability of rubber* to gases are described. The subjects are discussed from a criticial point of view, with many original references, and certain new points of view are introduced. *Stability toward O* is of great importance in its influence on the life of rubber, but *accessibility of O* is sometimes of equal or greater importance. Balloon fabric may be stable for yrs. in darkness, but on exposure of one side to O for a few seconds, O passes through without chem. combination to the other side. In this case stability is the predominant factor. When rubber is heated, its rate of combination with O increases more rapidly than the diffusivity, and a condition is reached where the rubber can combine with more O than is available. Under such conditions, when 2 rubber mixts. are equally stable, the one in which O diffuses more rapidly deteriorates the more rapidly, whereas the 2 mixts. deteriorate at the same rate at a lower temp. These conditions apply to the 70° air oven test, where the rate of deterioration is increased about 180 times and the permeability only 5 times. In *aging tests with O under pressure at elevated temps.,* the concn. of O must be increased disproportionately to increase the rate of deterioration, and the increase of the concn. of O probably does not take the place of time for uniform penetration and leads to uneven oxidation. There is much to recommend a low concn. of O with slower deterioration, as in the Bruni test (cf. *C. A.* **16**, 4093). The effect of an *antioxidant* on the accessibility of O depends upon whether it acts as an antioxygen, as defined by Moureu and Dufraisse, or is merely a preferential reducing agent. The latter would be very limited in its protective action at normal temps., whereas it would be effective in protecting rubber for short periods against high temps., as in dry heat cures, in hot water bottles, or in accelerated aging tests where accessibility of O plays an important part. A general discussion follows the paper. C. C. DAVIS

Softeners and antisofteners. ERLE C. ZIMMERMAN AND LESLIE V. COOPER. *Ind. Eng. Chem.* **20**, 812–3(1928).—By measuring the plasticity of rubber before and after the addn. of a substance, the whole procedure being carried out under standardized conditions, it is possible to judge whether the substance softens or stiffens a rubber mixt. The *relative effects of different softeners and stiffeners* may also be detd. by this method. Stearic acid, pine tar, liquid asphalt, pine oil and degras showed the greatest softening action of 14 softeners tested, while benzidine and *p*-aminophenol are among the substances found to have a distinct stiffening action. C. C. DAVIS

Machine for testing rubber products used to absorb vibration. FRANZ D. ABBOTT. *Ind. Eng. Chem.* **20**, 853–7(1928).—A machine, termed a *compression flexometer,* for judging the resistance of rubber to prolonged vibration by its resistance to flexure while under compression is described and illustrated. Tests of rubber for shock insulators, motor supports and other objects which absorb vibration or undergo flexure while under compression show that the new method is a reliable indication of the behavior of the rubber in service. This is not true of elongation, tensile strength modulus and hardness tests or of static compression-set tests. C. C. DAVIS

Plasticity and elasticity of rubber. A. VAN ROSSEM AND H. VAN DER MEIJDEN. *Rubber Age* (N. Y.) **23**, 438–40(1928).—See *C. A.* **22**, 3063. C. C. DAVIS

The variability in the plasticity of plantation rubber. F. L. ELLIOTT. *Trans. Inst. Rubber Industry* **3**, 468–79(1928).—The expts. are a part of the Ceylon Rubber

Research Scheme. Comparative tests of the plasticity of raw rubbers, the same rubbers after mastication and after mixing with S showed that in most cases there is a definite relation between the plasticity of a raw rubber and its plasticity after mastication. With normal estate rubber, the plasticity of rubber-S mixts. was about 1.7 times that of the corresponding masticated rubber, but with special types, *e. g.*, sprayed latex rubber, this relation was not true. The rubbers were masticated with the same consumption of power in all cases, and the plasticity detns. were made on a Williams' plastimeter, and on a newly devised *extrusion plastimeter*, the construction and operation of which are described and illustrated. The vol. of rubber extruded per unit time is inversely proportional to the abs. viscosity, so D_{30} (de Vries) is inversely proportional to the 4th root of the vol. extruded. This extrusion method is therefore far more sensitive to differences of plasticity than is the parallel plate method, *e. g.*, 10% difference between D_{30} values (less than 0.1 mm.) corresponds to approx. a 45% difference in the rate of extrusion. With this procedure, it was found that the difference between the max. and min. values of crepe or of sheet is much greater than the difference between the mean values of the 2 types of rubber, *i. e.*, the differences in plasticity which depend upon the methods of prepn. of crepe and sheet are much smaller than those between individual samples. Sprayed latex rubber varied considerably and fine hard para was harder and less variable than crepe or sheet. The rate of vulcanization varied with the plasticity, the harder the rubber the more rapid its rate of vulcanization. By maturing rubber for different times, it was found that the state of maturation plays the predominant role in governing plasticity, an increase of maturation so slight that little change in the rate of cure was manifest, hardening the rubber 50%. The high values obtained by de Vries (*Mededeelingen* No. 46) for the viscosity of maturated rubber with little change in the D_{30} values are contrary to experience of the Ceylon Research Scheme. The plasticity changes on keeping, and perhaps this accounts for the conflicting results. Machine-dried crepe averaged approx. 25% more plastic than that dried at av. temps., so that the temp. of drying influences the plasticity. Thus rubber dried at 180° F. was about twice as plastic as rubber dried at 140°. The smoking process also increases the plasticity. A general discussion follows the paper.
C. C. DAVIS

Snow-white and bright-colored, non-poisonous, highly elastic rubber varnish with titanium dioxide. RUDOLF DITMAR. *Chem.-Ztg.* **51**, 506–7(1928).—TiO_2 gives excellent results when used as a pigment in white and bright-colored rubber varnishes.
C. C. DAVIS

The effect of antioxidants on the color of rubber mixes. T. L. GARNER. *Trans. Inst. Rubber Industry* **3**, 417–27(1928).—Systematic tests of the color produced by antioxidants in different colored rubber mixts. were carried out. Preliminary tests showed that the same effects are manifest in cured and uncured mixts., so in most cases uncured mixts. were used. They were maintained (1) in air in darkness; (2) in air in daylight and (3) in N in daylight. The results show that in general uncured and cured rubber mixts. contg. antioxidants become discolored on exposure to daylight in air or in an inert gas, whereas there is little or no effect when they are kept in darkness in air. The color effect is only on the surface. The antioxidants tested were all aldehyde-amines, and the amine constituent may be responsible for the undesirable effects. Therefore the introduction of antioxidants of quite different chem. nature might furnish antioxidants which can be used in light-colored rubber products. C. C. DAVIS

The coloring of cold-cured rubber. W. E. SANDERSON. *Rubber Age* (N. Y.) **23**, 379–81; *Trans. Inst. Rubber Ind.* **4**, 22–39(1928).—See *C. A.* **22**, 3066. C. C. DAVIS

Reclaimed rubber. HENRY P. STEVENS. *Bull. Rubber Growers' Assocn.* **10**, 425–32(1928).—A review and discussion of recent developments and of the present economic situation. C. C. DAVIS

Vulcanization of rubber. NICHOLAS BACON. Cornell Univ. *J. Phys. Chem.* **32**, 801–27(1928).—A review of theoretical and exptl. work on the nature of vulcanization indicates that there are at least 4 possible assumptions, that (1) "combination" of rubber and S is simply the formation of a solid soln., in which case it should be possible to ext. S by treating a vulcanizate with excess raw rubber in a suitable solvent; (2) vulcanization is simple adsorption or absorption accompanied by a chem. reaction, in either of which cases a vulcanizate should be heterogeneous and it should be possible to fractionate it by peptization in C_6H_6 and thus obtain fractions with different S contents; (3) the compn. or structure of rubber is altered by vulcanization, combination with S being only a secondary reaction, in which case it should be possible to induce vulcanization without the vulcanizing agent taking a part, and also to obtain raw rubber from vulcanized rubber; or (4) the rubber mol. is very large and forms a series of compds. with S, the larger the mol. the smaller the differences between 2 successive compds. and the more difficult their sepn. In the present work, these 4 theoretical possibilities were investigated experimentally to ascertain which is the most probable explanation of

vulcanization. To test (1), hard rubber was extd. with acetone and was then heated to 190° with aniline contg. raw rubber in excess of that in the hard rubber. Though S is very sol. in aniline under these conditions, no S was extd. from the hard rubber, showing that "combined" S in hard rubber is more firmly held than in ordinary solid solns. According to (2), it should be possible to obtain soft vulcanized rubber from a mixt. of hard rubber and raw rubber provided their mutual adsorption could be effected, but after heating 15 parts of hard rubber with 85 parts of raw rubber at 150°, the 2 components could be sepd. by peptization in C_6H_6. Likewise heating at 180° or 245° a mixt. of hard rubber and of excess raw rubber, each peptized in aniline, failed to yield a vulcanized product, and from the product obtained by evapn. the hard rubber was recovered by C_6H_6 (cf. *J. Soc. Chem. Ind.* **13**, 14(1894)). Similarly, when a mixt. of hard rubber and raw rubber in xylene was refluxed, the raw rubber was sepd. from the solid product by peptization in C_6H_6. The addn. of vulcanization accelerators and ZnO to mixts. of hard rubber and raw rubber, either in the solid state or peptized, did not bring about vulcanization. In the fractional peptization tests, mixts. contg. much less combined S than those of Stevens (*C. A.* **13**, 3039) were used to ascertain whether even under such conditions homogeneity persisted. Rubber cured with different proportions of S was extd. with acetone and was then peptized in hot C_6H_6 and successive fractions were analyzed. All samples were homogeneous, including those which contained less than 0.1% "combined" S. With the aid of ultra-accelerators and ZnO, samples, which from a phys. point of view were well cured, were obtained which contained less than 0.5% S. Removal of protein did not influence the results with mixts. of raw and cured rubber. Further vulcanization tests showed that when coeffs. of vulcanization are very close together, *e. g.*, 0.37 and 0.57% combined S, homogeneous mixts. cannot be obtained by heating them in peptized form. Homogeneous products were also obtained when mixts. cured below the m. p. of S were extd. with acetone and then peptized in C_6H_6. Accordingly even below its m. p., S is sol. in rubber. When sheet rubber was heated with a layer of S on one side, the surface in contact with S had a much higher coeff. of vulcanization than the part farthest from the S, and on fractional peptization fractions contg. different proportions were obtained. This proves that rubber is not composed of "giant" mols. Boiling BuOH does not peptize rubber but dissolves S, so that equil. between resin-free rubber and S was studied in this solvent at 117°. Different concns. of S, *i. e.*, different proportions based on the rubber, were used, and after drying *in vacuo* and extg. with acetone, the S content was detd. In all cases the rate of increase of S content diminished progressively until ultimately it became so slow that it could not be decided whether equil. had been reached or whether diffusion became so slow that the reaction was inhibited. The data show no evidence whatever of the formation of a chem. compd. up to the *compd.*, $C_{10}H_{16}S_2$, which was formed in each case when sufficient S was present. The proportion of S combining with the rubber was practically proportional to the concn. of S. Because the soly. of S in rubber increased with increase in the coeff. of vulcanization, which in turn was counteracted by the lowered diffusion, there was probably a static condition reached which was a false equil. The results as a whole show that the *union between rubber and S is chem.*, and that the theory of C. O. Weber is in modified form the most satisfactory for explaining vulcanization. Since fractional peptization shows that homogeneity exists even with a coeff. of vulcanization of 0.1%, the initial compd. of the Weber series must be wrong. The *mol. wt. of the rubber hydrocarbon* is at least 32,000 to account for the initial compd. of a series extending to a compd. contg. 32% S. This compd. would be $(C_5H_8)_{470}S$, and if analytical methods were more delicate, it might be found that homogeneity existed below 0.1% S, in which case the value of n in the initial compd. $(C_5H_8)_nS$ would be even greater than 470. C. C. DAVIS

Industrial motor applications in the rubber industry. A. P. REGAL. *Elec. J.* **25**, 395–9(1928).—Profusely illustrated. C. G. F.

The aging of rubber. Its preservation. F. JACOBS. *Caoutchouc & gutta-percha* **25**, 13,964–5, 14,079–82(1928); cf. *C. A.* **22**, 1057.—A general review and discussion of present developments. C. C. DAVIS

The colloid chemistry of rubber. J. DUGUÉ. *Rev. gén. caoutchouc* **1928**, No. 43, 3–6.—The importance of colloid chemistry in the study of rubber is discussed. C. C. DAVIS

Has the synthetic dye industry been of aid in the development of the rubber industry? ANDRÉ DUBOSC. *Caoutchouc & gutta-percha* **25**, 14,000–2(1928).—A general discussion, suggested by a recent article of Powers on the same subject (cf. *C. A.* **21**, 497). C. C. DAVIS

The application of paint and varnish to rubber products. A. LINZ. *Trans. Inst. Rubber Industry* **4**, 59–67(1928).—A review and discussion of present developments and problems. C. C. DAVIS

Synthetic rubbers. L. Sloïm. *Rev. gén. caoutchouc* **1928**, No. 43, 7–8; cf. *C. A.* **22**, 1061.—A further discussion of the chem. constitution of rubber. C. C. Davis

Investigations on the structure of rubber. Paul Bary and Ernst A. Hauser. *Rev. gén. caoutchouc* **1928**, No. 42, 3–11.—The paper is a reconciliation of the previously independent and divergent views of B. and of H. Three problems have marked the general course of expts. up to the present: (1) the *existence of 2 components;* (2) the *conversion of 1 component into the other*, and (3) the *structure as judged by x-ray examn.* At present there is confusion over the *nomenclature of the 2 components of rubber*, and it is strongly recommended that the term *α-rubber* for the Et_2O-sol. component and the term *β-rubber* for the Et_2O-insol. component be adopted. The difference between α- and β-rubber lies chiefly in the fact that in α-rubber the primary valence chains (united in bundle form by secondary valences) are smaller than in β-rubber. A discussion of the relation of the most recent work on the viscosity of rubber solns. in its relation to the *reversible transformation of* α- and *β-rubber* indicates that the 2 components are in equil. under conditions similar to those of a jelly. To do away with the confusion existing in the subject of the no. of phases in a rubber system, the attempt is made to define precisely the *concept of a jelly and a gel.* Unstretched rubber is a jelly, *i. e.*, a soln. or homogeneous system of 2 or more rubber polymers. Stretching of rubber causes a swelling and transformation into a gel. A gel is a substance which consists of at least 2 phases, where the degree of dispersion of 1 phase in the other is of little significance. The results already obtained with x-rays are discussed, attention being called to the false conclusions which may easily be drawn from x-ray data. As a result of the review and discussion, certain conclusions may be drawn regarding the structure of rubber. Rubber contains 2 components of the same elementary chem. compn. but of different degrees of polymerization and of differing fluidity. The component with the greater fluidity is the one with the lower degree of polymerization. The proportions of these 2 components vary so that if α and β are the mean values of the degrees of polymerization and n_1 and n_2 are the nos. of mols., resp., then the ratio $n_1\alpha/(n_2\beta)$ varies with the temp. and with the mech. treatment. At ordinary temp. and at temps. a little lower, the value of $n_1\alpha/(n_2\beta)$ is very low for rubber at rest, but it is increased by work and heat, *e. g.*, by repeated stretching. The fact that "frozen" rubber in an unstretched condition gives Debye-Scherrer-Hull rings, where the proportion of β-rubber has increased at the expense of the α-rubber, indicates that the less diffusible component is responsible for the x-ray diagram. In the elongation of normal rubber (not "frozen"), the α-component, which is dissolved in the β-component to form a jelly (by the definition proposed), seps. as a result of the negative internal pressure produced by the elongation, and the jelly is transformed into a gel (2-phase system). In the elongation of "frozen" rubber, there is a return to the normal form, as occurs when rubber is heated. Rubber contains therefore a sort of network of solid β-component which during elongation of the rubber assumes the form of a bundle of parallel fibers. That these filaments exist is confirmed by the "crystn." expts. of Pummerer and Koch (*C. A.* **18**, 3737) and Feuchter (*C. A.* **19**, 2576), by the freezing expts. of Hock (*C. A.* **19**, 3036) and by microscopic examn. of rubber solns. during evapn. by Bary (*Rev. gén. caoutchouc* **4**, No. 31, 7(1927)). An x-ray diagram is formed only when the β-component is condensed sufficiently, *i. e.*, when the chains of C atoms have only a slight freedom of oscillation. This condition exists when the proportion of β-component is increased by freezing or when it is condensed by elongation. Also in *Kautschuk* **1928**, 96–102 but without x-ray diagrams. C. C. Davis

Balata rubber. A. D. Luttringer. *Caoutchouc & gutta-percha* **25**, 14,036–9, 14,076–9(1928).—The characteristics of balata and its production in various localities are described. C. C. Davis

Power consumption in the preparation of crepe rubber. M. Schröter and R. Riebl. *Med. Proefsta. Rubber, Buitenzorg*, **1927**, No. 22; *Arch. Rubbercultuur* **11**, 397–419(1927). E. H.

Some notes on factory procedure and efficiency, especially in reference to crepe manufacture. T. E. H. O'Brien. *Trop. Agr.* (Ceylon) **70**, 351–61(1928).—Formic acid is as satisfactory as acetic acid for coagulating latex. When milky serum is discarded, as is usually done, the value of the rubber lost is frequently greater than that of the acid necessary to coagulate it. Sufficient acid should always be added to produce a clear or only slightly cloudy serum. The proportion required varies with the individual latex and is not always proportional to its rubber content. Diln. of latex to 2 lb. per gal. provides a coagulum of the right consistency for maceration. *p*-Nitrophenol prevents mold formation on smoked sheet if properly used. If it is added directly to latex in a proportion greater than 1:4000 of rubber, discolored crepe will result. In the proportion mentioned, no discoloration was observed in most tests. However, fungal spots developed when the crepe was subjected to severe tests. Under

ordinary conditions of manuf. and storage, it is thought this proportion should prevent spotting.

A. L. MEHRING

Swelling phenomena. The swelling of rubber. P. STAMBERGER. Univ. College London. *Kolloid-Z.* **45,** 239–44(1928); cf. *C. A.* **22,** 2078, 3065.—When a gel of unmilled pure rubber is removed from a solvent and is placed in the satd. vapor of the solvent, equil. is displaced and the imbibed liquid is exuded. The forces which are responsible for this absorption of part of the solvent are no longer active, and the elastic pressure of the gel walls acts in opposition to these forces, so that the process is reversible. By regarding the exudating action as analogous to a flow of liquid through a capillary, expressions are derived for the *forces causing the exudation.* The nature of these forces is not explained. The *rate of exudation* depends upon the temp., solvent and previous history of the gel. The lower the temp., the greater the rate of exudation. The rubber from the gel is less elastic and its behavior toward solvents is no longer the same as before. With solvating solvents like C_6H_6 or PhMe, this change is so pronounced that when the liquid is exuded the gel liquefies, and swells in an unrestrained way, forming viscous solns. This lends doubt to the *existence of 2 phases in rubber.* The change in the gel is less marked with solvents of the benzine and Et_2O type. Since the gels are no longer in equil. after removal from their solvent into the satd. vapor, there must be a difference between *swelling in liquid and swelling in satd. vapor.*

C. C. DAVIS

The destruction of the hydrocarbons of raw rubber by fungi. O. DE VRIES. Rubber Expt. Sta., Breitenzorg, Java. *Centr. Bakt. Parasitenk. II Abt.* **74,** 22–4(1928).—Fresh raw rubber contains about 93% hydrocarbons. The loss when infected with fungi may be as much as 22% in 2 years and 30% in 5 years. The viscosity is also markedly decreased.

JOHN T. MYERS

New method of evaluation of the quality of fillers in rubber manufacture. M. PAVLENKO AND P. NAZAROV. *J. Chem. Ind.* (*Moscow*) **4,** 642–50(1927).—Since the quality of rubber products depends not only on their quant. chem. compn. but also on the phys. condition of the components of the colloidal system involved the question arises, by what analytical method can the latter be detd. Several investigators sought to approach this problem by measurements of the size of the particles of the fillers, and Thies (*C. A.* **20,** 310) by detg. the adsorption capacity of fillers toward dyes in aq. soln. The authors propose a different method of detg. the quality of a filler from the point of view of its influence on the strength of the rubber. It is based on the interrelation which exists between the viscosity (internal fraction) of a colloidal system consisting of rubber, solvent and filler, the degree of plasticity of the system when devoid of solvent, and finally its degree of elasticity and strength after vulcanization. The viscosity of the system rubber–solvent–filler depends on a number of factors, such as the kind of rubber and its phys. condition, the nature of the filler and the size and shape of its particles, the nature of the solvent, the concn., the duration of interaction and the temp. If the filler is varied and all other conditions are left unchanged, each filler imparts to the system a characteristic viscosity. For the first series of experiments 5 different brands of C blacks were used as fillers. A large quantity of a 5% rubber soln. in xylene was prepd. and portions of this soln. were taken for each subsequent expt., which consisted in stirring 25 g. of a particular brand of C black with 500 cc. of the rubber soln., pouring the mixt. in a glass cylinder 26 cm. long and 26 mm. in diam., placing it in a thermostat at 25° and measuring its relative viscosity at regular intervals. Viscosity measurements were made by detg. the time (in sec.) required by a glass ball 6 mm. in diam. to drop from the surface of the viscous mass to the bottom, and dividing this figure by the time required in a blank test for the ball to pass through an equal layer of the rubber soln. contg. no C black. The ratio obtained was the *relative viscosity* of the system rubber–zylene–C black. It was found that the viscosity of the blank soln. did not appreciably change in the course of time, whereas that of the system containing C black underwent considerable changes. These changes enabled the authors to draw a curve of relative viscosity as a function of time for every particular C black. During the first 24 hrs. the viscosity gradually increased, until the curve reached a max. and after a certain turning point it began to drop. Each particular brand of C black gave a characteristic curve. Presumably the initial increase in viscosity depends upon the fact that a uniform mixt. of C black with rubber soln. is not attained at once, the mixt. being at first flocculent in spite of being stirred with a glass rod; the flocculency gradually decreases and, by the time it almost disappears, the max. relative viscosity is reached, after which the curve begins to drop, due to disintegration of the rubber. Expts. confirmed the theoretical considerations, according to which the C black brands which produced the highest relative viscosity (at the turning point) in rubber solns. gave the strongest vulcanizates, as seen in the following table. It is remarkable that the better the brand of C black, the longer its mixt. with rubber

C Black brand	Relative viscosities at turning points	Strength in kg./cm.² of vulcanizates
Microne	2.54	225.4
G. E. T. No. 3	2.36	209.7
G. E. T. No. 5	2.10	195.6
Dutch	1.95	188.1
Dure	1.72	173.8

soln. remained flocculent. This observation alone can be used as a fairly reliable guide in detg. the value of a given filler, but relative viscosity detns. give surer results. In expts. carried out in the same manner with various brands of *kaolins* and of chalks as *fillers* instead of C black, the results were about the same. BERNARD NELSON

The thermochemistry of rubber. SIEGFRIED BOSTRÖM. Univ. Giessen. *Kolloid-chem. Beihefte* **26,** 439–70(1928).—The work consists of 3 parts: (1) the development of a method for detg. the "activity" of technical pigments and filler; (2) the thermodynamics of the Joule effect in rubber and (3) an investigation of the thermochemistry of the vulcanization process. The "activity" of fillers, *i. e.*, their so-called reinforcing effect, was detd. indirectly by measuring 3 heat effects: (1) the heat of swelling of rubber in C_6H_6; (2) the heat of wetting of the powder by C_6H_6 and (3) the energy represented in the adhesion of filler and rubber. The energy was then calcd. on a basis of 1 g. of C black from the difference between (1) and the sum of (2) and (3). The values of (3) for different fillers is considered to be a criterion of their "activity," particularly since the actual results obtained conform to the relative effects obtained by Wiegand in a quite different way (cf. *C. A.* **14,** 2732). Preliminary tests showed that the heat of wetting of C blacks increases with their sp. surface. In studying the thermodynamics of the Joule effect, the change in total energy, the work of extension and the temp. coeff. of the mech. work were detd. The heat tone was directly proportional to the elongation, lending support to the theory that the Joule effect depends upon a fiber structure. From the point of view of the Hock theory (cf. *C. A.* **21,** 4092) the Joule heat of elongation is proportional to the no. of aligned and packed particles. The sp. heat of raw rubber, detd. by 3 different methods, averaged 0.37 at 17° and the temp. coeffs. of mech. work involved in stretching to 250, 500 and 800% elongation were —0.002, —0.0024 and —0.0035 cal. per degree C. The heat tone of the reaction between S_2Cl_2 and rubber dissolved in benzine was measured through a range of concn. of 0–1.3 g. of S_2Cl_2 per g. of rubber, but no definite conclusion could be drawn as to whether adsorption or chem. combination was involved. The app., which comprised a specially constructed *calorimeter*, and the technic are described in detail and illustrated. C. C. DAVIS

Rubber in the printing industry. D. R. SCHLITZ. Goodyear Tire & Rubber Co. *Rubber Age* (N. Y.) **23,** 619–20(1928).—An illustrated description. C. C. DAVIS

Evaluation of variable temperature cures. J. R. SHEPPARD AND W. B. WIEGAND. Eagle-Picher Lead Co., Joplin, Mo., and Binney & Smith Co., New York. *Ind. Eng. Chem.* **20,** 953–9(1928).—Utilizing the generally accepted empirical rule that the intensity of the curing action becomes twice as great for each 15° F. rise of temp., formulas are derived to show the relations between the several variables of a cure segment with a const. temp. gradient, *viz.*, the intensity of curing action, the curing effect, the time and the temp., on the one hand and the consts. of such a cure, *viz.*, the initial temp. and the temp. gradient, on the other hand. An exact valuation of cures is applied to schedules with variable temps. by the use of the equations showing the curing effect as a function of the other characteristics of the cure. These equations are the most important ones in practice. The curing effect, which measures the net value of a schedule in effecting vulcanization, can be detd. for a given schedule by calcn. from one of the "effect" equations, by reading directly from graphs which are given, or by estg. the area under an intensity-time curve. The intensity of curing action is a measure of the importance of a temp. in inducing vulcanization, and the intensity-time curve shows the curing ability of the various parts of a schedule even more accurately than the more usual temp.-time curve. Examples of the application of the method to typical factory cures are given. C. C. DAVIS

Chromolited rubber molds. F. E. RICHARDSON. Nat. Chromium Corp. *Rubber Age* (N. Y.) **23,** 607–8(1928).—When molds are properly plated with Cr, there is less sticking of the rubber than to other metals because of the unusual resistance to heat and to attack by acids and gases. C. C. DAVIS

The use of mineral oil with a favorable customs duty in the rubber industry. PAUL ALEXANDER. *Gummi-Ztg.* **42,** 2410–1(1928).—A discussion dealing with the definition of *solvent for rubber*. C. C. DAVIS

Abrasion tests of rubber stocks containing various types of carbon black. W. B.

PLUMMER AND D. J. BEAVER. *Ind. Eng. Chem.* **20**, 895–9(1928).—On a slightly modified Williams abrasion machine (cf. *C. A.* **21**, 2573) the resistance to abrasion of rubber mixts. contg. different types of C black decreased with increase of the particle size of the abrasive up to 0.45 mm., above which the resistance to abrasion increased. No explanation is offered. Rubber mixts. were then alternately abraided and aged in air at 70° so that only the surface which had deteriorated was worn away. In this way an indication was obtained of the resistance to abrasion of the mixts. under conditions more nearly approaching service conditions, where abrasion and aging progress simultaneously. Some types of C black increased the rate of deterioration much more than did other types, as a result of which the relative resistances to abrasion of mixts. contg. different C blacks changed as aging progressed, in fact the resistance to abrasion of the surface layers of one mixt. may be greater than that of another mixt. before aging but may become less than that of the other after aging. This shows that the value of a C black must be judged not only by the resistance to abrasion but also by the aging properties which it imparts to rubber. Where the wear is slight compared with the deterioration, the aging imparted by a C black is a determinant factor in the life of a tire. C. C. DAVIS

Rubber compression testing machine. C. L. HIPPENSTEEL. Bell Telephone Labs. *India Rubber World* **78**, 55–6(1928).—See *C. A.* **22**, 2855. C. C. DAVIS

Carbon black. I. A study of its volatile constituents. C. R. JOHNSON. G. L. Cabot, Inc., Boston. *Ind. Eng. Chem.* **20**, 904–8(1928).—Complete analyses were made of 5 types of C blacks, before and after evacuation, and of the gases removed, and a C balance was detd. with the object of correlating the proportion and compn. of the volatile components and the properties imparted to vulcanized rubber mixts. by the blacks. The results show that within certain limits the volatile matter in a C black has no determinant effect on the properties imparted to rubber, but that above certain limits it reduces the reënforcing power of the C black and retards the rate of vulcanization. This undesirable limit is fairly const. for each grade of C black, but the limits vary among different blacks. The gases extd. from the C blacks contained CO, CO_2, H, N, CH_4, C_2H_6, illuminants and O. It is probable that the CO and CO_2 were reaction products of the O originally present. C. C. DAVIS

Legal specifications concerning the color of rubber goods. A. BEYTHIEN. *Gummi-Ztg.* **42**, 2464–5(1928).—Of special concern to German industry. C. C. DAVIS

The influence of Vulkan colors on the aging of rubber articles. RUDOLF DITMAR. Kautschuklaboratorium, Graz. *Gummi-Ztg.* **42**, 2519(1928).—A large no. of "Vulkan" colors were tested in the 2 different base mixts. to det. the influence of the individual colors on the aging of the mixt. Some of the colors caused abnormally rapid deterioration, whereas others had a distinctly preservative effect. Whether the color had a good or a bad effect depended in turn upon the type of rubber mix. C. C. DAVIS

A scheme of accelerator classification. R. P. DINSMORE AND W. W. VOGT. *Trans. Inst. Rubber Industry* **4**, 85–106(1928).—A survey and crit. discussion of the *characteristics of org. accelerators*, which for convenience may be divided into several groups: (1) dithiocarbamates; (2) xanthates; (3) thiuram mono- and disulfides; (4) mercaptobenzothiazoles; (5) aldehyde-amines; (6) ethylideneanilines; (7) guanidines; (8) thioureas, and (9) individual cases, such as *p*-nitrosodimethylaniline, aldehyde-ammonia, hexamethylenetetramine and the CS_2 reaction product of butyraldehydeaniline, of which other accelerators of the same types are not known. Summarized data show the general characteristics of these groups, including their *relative activity and characteristics during manufacturing processes*, their *S requirements*, the *phys. properties which they impart to vulcanizates*, their *stability during vulcanization*, their *antioxidant properties* and their *stearic acid requirements*. The chem. compns. of 46 com. accelerators are also tabulated. In manufacturing, accelerators should be judged by (1) their activity; (2) their ability to disperse and to soften rubber mixts. and not cause scorching; (3) their stability in uncured mixts.; (4) the S requirements; (5) the necessity for stearic acid; (6) their adaptability to air, steam and press curing; (7) their stability during vulcanization; (8) the stiffness and tensile properties imparted to rubber mixts. with and without pigments; (9) their antioxidant power and (10) the changes such as stiffening in vulcanizates contg. the accelerators. These criteria are discussed individually, in some cases with the inclusion of new data. A study of the *difference between tearing by hand and max. tensile product as a criterion of proper cures* showed that with mixts. contg. no pigments and particularly when unaccelerated, there is a big difference between the optimum cures, tearing by hand indicating a shorter cure than max. tensile product. With loaded mixts. these differences become relatively small. The max. resistance to tearing by hand is claimed to coincide in all cases with the cure which ages best. The *rate of oxidation of a rubber mixt. during natural or artificial aging* increases progressively with the time of vulcanization and bears no relation to the flatness of the

tensile strength-time of vulcanization curve, so that constancy of tensile strength over a range of time of vulcanization is useless in judging the aging properties imparted by an accelerator to a rubber mixt. The *tendency of a rubber mixt. to scorch* may be judged by heating for definite periods at 70° or 100° and detg. the plasticity and recovery in a Williams plastimeter before and after such heating. *Stiffening during aging* is not necessarily accompanied by an increase in combined S, and may be simulated artificially by heating rubber mixts. at 70° in an inert gas. Numerous examples are cited to show the behavior of some of the more important individual accelerators. A general discussion follows the paper. Also in *Rubber Age* (N. Y.) **23**, 554–7(1928). C. C. DAVIS

Watch case vulcanizers. JOSEPH ROSSMAN. *India Rubber World* **78**, 69–71 (1928).—A chronological review of the patent literature. C. C. DAVIS

Priestley, the English godfather of rubber. A. DUBOSC. *Rev. gén. caoutchouc* **5**, No. 44, 7–8(1928).—Historical sketch. C. C. DAVIS

"Mineral rubber." An historical point. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **25**, 14,157(1928).—Old references to "mineral rubber" are cited to show that the term has been in use for many years. C. C. DAVIS

Mechanical tests of rubber and probabilities. R. FRIC. *Chimie et industrie* **Special No.**, 541–6(April, 1928).—A mathematical discussion based on the results obtained in tensile tests of 732 test samples as nearly the same as they could be made. A. PAPINEAU-COUTURE

Methods for controlling changes in rubbers. J. VILLEY AND P. VERNOTTE. *Chimie et industrie* **Special No.**, 534–6(April, 1928); cf. *C. A.* **19**, 1208.—A discussion of the conditions which should be fulfilled by methods for following and estg. quantitatively the changes in rubber on aging. Two of the important requirements insisted upon are that the test sample should not be destroyed so that the change in the rubber may be followed right through on the same sample, and that the results should be capable of numerical expression. Two methods are suggested as suitable, a torsion test, and a dielec. test (*C. A.* **18**, 2617). A. PAPINEAU-COUTURE

The development of rubber reclaiming since the War and its importance in the economics of rubber. PAUL ALEXANDER. *Gummi-Ztg.* **42**, 2796–8(1928).—Historical. C. C. DAVIS

Present researches in the rubber industry. ANDRÉ BLOC. *Science et industrie* **12**, No. 170, 37–41; No. 174, 47–9.—An illustrated review and description, dealing with new methods and improvements in the *prepn. of raw rubber*, the *electrolysis of rubber*, the *use of concd. latex, synthetic rubbers, org. accelerators, antioxidants* and the *manuf. of reclaimed rubber*. C. C. DAVIS

Investigations on the structure of rubber. PAUL BARY AND ERNST A. HAUSER. *Rubber Age* (N. Y.) **23**, 685–8(1928).—English version of the article in *C. A.* **22**, 4005. C. C. DAVIS

The hardness testing of vulcanized rubber. T. R. DAWSON. *Trans. Inst. Rubber Industry* **3**, 217–33(1927).—A crit. survey of various methods of measuring the hardness of rubber, with a description of the principles and technic of the *durometer, plastometer* and *scleroscope* types of app., with references to the literature on the subject. In tests of different rubber mixts. at different temps. (60–80°F.) with a Shore scleroscope, the rebound increased in direct proportion to the increase in temp., and decreased with increase in the time of cures. The magnitude of this increase with temp. varied greatly with the compn. of the mixt. The variation with time of cure was of minor importance; the scleroscope measures primarily the resilience and is useless for detg. the state of cure. In general with increasing proportion of filler or pigment, the resilience decreased progressively, in direct contrast to metals where the harder the metal the greater the scleroscope rebound. *Application* for the first time *of the Herbert pendulum to rubber* showed that the time of swing decreased with increase in the proportion of fillers or pigments, *i. e.*, with increase in hardness, again in contrast to the behavior of metals. A graphical *comparison of plastometer and scleroscope tests* showed an essentially linear relation between the 2 series of values, while the proportional changes depended upon the filler or pigment. In conjunction with previous work, the expts. indicate that the fundamental factors governing dynamic indentation tests also play the chief role in static indentation tests. C. C. DAVIS

The effect of heat on raw rubber in the presence and absence of air. J. D. FRY AND B. D. PORRITT. *Trans. Inst. Rubber Industry* **3**, 203–16(1927).—Mech. working, heat and atm. O are all responsible for the phys. changes accompanying milling. Of these mech. work and heat are already considered to be responsible for the plasticizing effect, and the influence of O has not been realized. The present paper shows the important *part played by O* and the different effects produced in its presence and absence. The effect on the soln. viscosity was first detd. by heating rubber in air at different temps. from 100° to 150°, under which conditions it was found that the

higher the temp. the lower was the subsequent soln. viscosity. Rubber milled to different extents was then heated in air at different temps. from 106° to 180° for different periods (30 min. to 4 hrs.), after which the soln. viscosities of the products were detd. By comparing the *effect on the soln. viscosity of the time of milling and the time of heating*, it was found that around 100° heating had relatively little effect, but above this temp. the effect of heat became greater and at 150° the curve of viscosity against time of heating closely approximated the curve of viscosity against time of milling. The chief effect produced by milling can therefore be duplicated by heating rubber at 150° for a few hrs. The curves were of an exponential character and suggested a *chem. reaction*, for which reason the expts. were repeated under identical conditions with different proportions of air and *in vacuo*, H, N and steam. *In vacuo*, H, N or steam there was little change in viscosity even after heating 4 hrs. at 150°, whereas in air the viscosity diminished with increase in the proportion of air. Thus with 1 g. of rubber in 9 cc. of C_6H_6, the viscosity was 469 with no O, decreased to 393 with 0.000046 g. of O, to 317 with 0.000103 g., to 160 with 0.000491 g., to 99 with 0.000989 g. and to 57.6 with an unlimited air supply. The results show that both O and heat are necessary to obtain the ordinary effect produced by milling, and that if the only change desired is reduction of the soln. viscosity, the results accomplished by milling may be reproduced by heating in the presence of O. The mechanism of this action of O and heat remains undetd. A general discussion follows the paper. C. C. DAVIS

Investigation of the structure of stretched rubber. LOTHAR HOCK AND WALTHER BARTH. *Z. physik. Chem.* **134**, 271–8(1928).—X-ray photographs of stretched synthetic Me rubber at —60° show interference bands with sharp edges and weak center indicative of a tendency toward line formation in nearly the same positions as the lines of stretched natural rubber. G. L. CLARK

Present knowledge of the constitution of the rubber molecule. S. C. J. OLIVIER. *Chimie et industrie* **Special No.**, 537–40(April, 1928).—A brief critical review of the various theories proposed as to the chem. constitution of the rubber mol. A. P.-C.

The orderly micellar structure of rubber. H. MARK AND G. v. SUSICH. I. G. Farbenindustrie A. G. *Kolloid-Z.* **46**, 11–21(1928).—When pieces or films of natural rubber are stretched greatly an orientation within the member takes place not only in the direction of stretch but in the directions at right angles to it. X-ray analysis of such a crystd. prepn. assigns the stretched rubber to the rhombic crystal system. The identity period of the elementary units is $a = 12.3$, $b = 8.3$, $c = 8.1$ A. U. The no. of isoprene residues in the elementary unit is 8. The crystal class is probably V or V_h. Possible crystal structures are discussed and a space distribution of the C atoms is proposed which brings into agreement the orientation of the primary valence chains in the direction of stretch, the somewhat altered atom spacing for the C=C and C=C linkages, and the observed intensities of the most important interference bands. Several chem. reactions are described, by means of which it was sought to convert stretched rubber into derivs. retaining the structure, much as is the case in a number of topochem. reactions of cellulose. The rubber derivs. gave the x-ray pattern for amorphous material. F. L. BROWNE

The two coagulations of latices. RENÉ AUDUBERT AND G. LEJEUNE. *Rev. gén. colloïdes* **5**, 713–22(1927).—Only fresh *Hevea* latex was used by de Vries when he proved that under certain conditions it can be coagulated twice in succession with an intermediate dispersed state. This suggested similar expts. with *Hevea* and *Landolphia* latices preserved with NH_3, and with p_H values much greater than those of de V. Excess NH_3 was first removed by evapn. *in vacuo*, giving a product with p_H of 9–10. In all cases the concns. of the acid solns. added were so adjusted that regardless of the quantity of acid, the vol. added made the new vol. twice the original vol. Redispersion and recoagulation are most distinct with *Landolphia* and AcOH. When the latex has a high rubber content, *viz.*, above 25%, coagulation is normal and increasing proportions of acid merely accelerate the single and final coagulation. When the latex contains 15–25% rubber, addn. of acid (1) first causes complete coagulation (clear serum), (2) then redispersion into the form of agglutinated globules, which pass through a max. condition, and (3) finally complete coagulation a second time. In latex contg. less than 15% rubber, the redispersion is still more pronounced and complete so that the mixt. becomes completely liquid again; nevertheless a second coagulation takes place with still more acid. Throughout the redispersion, the elec. charge on the granules remains negative, so that the redispersion cannot be explained by an electro-capillary inversion of the globules, the concn. of acid at the time corresponding to the isoelec. point of rubber. When casein or gelatin is first added to the latex, coagulation is still abnormal, though different insofar as the same charges occur at lower p_H values. With casein or gelatin, the first agglutinated aggregates have a negative charge, whereas the flocculates of the second coagulation have a positive

charge. The p_H corresponding to this inversion of charge is not near the isoelec. point of the protein (4.7) but is more strongly acid, *viz.*, 2–3. This suggests that the casein or gelatin envelops the rubber globule so that the inversion of the charge of the micelles comprising this protective film governs the inversion of the charge of the globule + film. The difference between the p_H of inversion and that of the isoelec. point of the casein or gelatin indicates that the charge of the rubber plays a part, but that the natural protein does not. The natural protein is sep. from the rubber globule (peptized) both in the original latex and during the period of redispersion, and can be removed by dialysis. Assuming that the isoelec. point of the natural protein is in the alk. region, a negatively charged latex globule adsorbs the protein micelles, the resultant, rubber-protein remaining negative. A small increase in H ions diminishes this charge, with adsorption of H ions. With further addn. of H ions the negative charge is so much reduced that agglutination and coagulation follow. With the addn. of still more H ions, the negative charge is so greatly diminished that the protein micelles are liberated and peptized and the coagulated rubber reverts to a state of agglutination. Finally with more H ions, the protein is coagulated and its network structure entraps the agglutinated globules, causing the second coagulation. C. C. DAVIS

Dispersoidological investigations of latex. P. P. VON VEIMARN. *Bull. Chem. Soc. Japan* **3**, 157–68(1928).—Latex preserved with NH_3, concd. latex (80% rubber) and vulcanized latex were used in the expts. In NH_3-preserved latex, particles of every shape described by previous investigators were found, the no. of ultramicroscopic particles being considerably greater than the no. of microscopic ones. A comparison of photomicrographs of *Hevea* latex and the latex of *Ficus elastica* and of gelatinous spherulites of cellulose (cf. *C. A.* **22**, 873, 4028) indicated that in some latexes emulsion-suspensions of gelatinous isospherulites are present, probably in the aggregate-fluid-cryst. state. The film surrounding the viscous internal fluid of latex particles is, contrary to Freundlich and Hauser, probably composed of a mixt. of rubber and protein particles. In conjunction with the works of previous investigators, it is concluded that latex is a polydisperse system of isoaggregate particles (isospherulites), the general consistency of which is fluid and gelatinous. The individual solid particles composing the isoaggregate particles are for the greater part invisible under the ultramicroscope. The components of the serum (the dispersion medium in which the isoaggregate particles are suspended), *viz.*, proteins, water, resins, etc., are present not only in the surface film but also inside the isoaggregates. The non-rubber components play corresponding roles in the changes in consistency and structure which the isoaggregates undergo during drying and other coagulation processes. The high elasticity of rubber depends upon the presence in the viscous liquid or gelatinous medium of solid structural elements which possess the ability to become spirally curled after release from tension. The *gelatinization of latex by extremely concd. aq. solns. of dispergators of proteins, e. g.*, LiI, LiSCN, $Ca(SCN)_2$, NaI, $Ca(NO_3)_2$, $CaCl_2$, polyphenols, pyrogallol, resorcinol, thiourea, guanidine thiocyanate, AcOH and KOH solns. and by *aggregators of proteins, e. g.*, Na citrate, KNa tartrate and K_2SO_4, was also studied. At suitable temps. and concns., dispergators cause almost immediate and complete gelatinization, with formation of a coherent jelly. This can for instance be brought about by agitating at room temp. an equal vol. of satd. aq. LiI or LiSCN with latex. The structure of these jellies is such that they have greater strength longitudinally than transversely, and the higher the temp. of formation the stronger they are. These coherent jellies show syneresis. Aggregators of proteins do not coagulate rubber in latex, at room temp., even after long standing, but by pouring latex into boiling concd. solns. and continuing the boiling, flaky coagula are obtained. By coagulation of latex through addn. of concd. solns. of silk, casein, chitin or keratin in aq. solns. of dispergators. coagula of mixed compn. are obtained, *viz.*, *rubber-silk*, *rubber-casein*, *rubber-cellulose*, *rubber-chitin* and *rubber-keratin*. The properties of these mixts. are under investigation. When vulcanized latex is gelatinized by the addn. of aq. solns. of dispergators, the jellies are weaker than those formed from raw latex, but by compression the tensile strength is increased. C. C. DAVIS

Plasticity determinations in crude rubber. VI. Changes in plasticity on keeping the rubber. O. DE VRIES. Proefstation voor Rubber, Nederlandsch-Indie. *Arch. Rubbercultuur* **12**, 411–9(1928) (Summarized in English 420–2); cf. *C. A.* **22**, 3316.—Various samples of smoked sheet and of pale crepe which had been kept for long periods were tested to det. changes in their plasticity, viscosity and vulcanizing properties. The results showed considerable variations, some rubbers changing much faster than others. Rubber 12 yrs. old was still in fairly good condition. C. C. DAVIS

Purification and fractionation of rubber. VII. RUDOLF PUMMERER, ALBRECHT ANDRIESSEN AND WOLFGANG GÜNDEL. Univ. Erlangen. *Ber.* **60B**, 1583–91(1928); cf. *C. A.* **22**, 886.—*I. Alkali purification of latex concentrate.*—As shown in the earlier

papers fresh latex and that preserved with NH_3 behave differently towards alkali. Expts. with the latex concentrate "Revertex" have further shown that the latex preserved with NH_3 has been altered in still another way. The statement of P. and Pahl that their "total rubber," obtained from NH_3-preserved latex with alkali, is protein- and N-free, needs correction. Even after most thorough and prolonged treatment with alkali at 50°, it still contains 0.15–0.4% N. On combustion with a reduced Cu spiral the C and H values add up to about 0.4% less than 100%, and as a substance with 0.4% of protein N should show a deficit of about 1% (because of the O present), the N remaining in this NH_3-preserved latex after purification with alkali must be amine N, evidently produced by the action of the NH_3 on the latex during the more or less protracted period of preservation. A gel rubber with 0.4% N refluxed 1 day in C_6H_6 with dil. NaOH yielded no amino acids (ninhydrin reaction) to the aq. alkali, nor did the rubber itself give the ninhydrin test when boiled with the reagent. On the other hand, ordinary "Revertex" yields a "total rubber" with only 0.04–0.1% N which is increased to 0.17% in the "gel rubber" remaining after the "total rubber" is extd. with Et_2O. A prepn. similar in properties to the repptd. gel rubber and still contg. 0.15% N can also be obtained by allowing the gel skeleton from crepe to swell in C_6H_6 and pptg. the clear C_6H_6 soln. after some weeks. "Sol rubbers" from crepe also often have a similar N content. *II. Fractional ether extn. of different latex and raw rubber prepns.*—Various rubber prepns. were extd. continuously in an app. which is described. (1) The extn. curve (with Me_2CO) for a purified "total rubber," prepd. from preserved latex with NaOH according to P. and Pahl, showed a distinct inflection after about 40 hrs. when 65–70% of the total rubber had dissolved, and after that there is very little further soln. (finally only 0.2–0.3% in 24 hrs.); the residue and these last slowly dissolving traces are apparently gel rubber, and as the soly. of the residue from the 10th to the 30th day remains practically const., the gel rubber, insofar as it dissolves, must be quite homogeneous. (2) The extn. curve for NH_3-preserved latex, such as used for the alkali purification for (1) but merely freed of H_2O-sol. substances by dialysis, then coagulated and extd. with Me_2CO, rises much more slowly than that for (1) and in 850 hrs. the quantity extd. is still far less than in (1) after 50 hrs. There is an inflection, but not so marked, in this curve also. (3) The curve for Para crepe is remarkably similar to the preceding curves. After 52% has been extd., very little more goes in soln. Such an Me_2CO-extd. crepe, freed of Me_2CO in a high vacuum, is not immediately suitable for fractional extn. with Et_2O as it swells up and breaks up into minute flocks which are carried over by the solvent, but after it has stood 3 months under CO_2 Et_2O exts. from it the sol rubber more rapidly and in larger quantity than originally (55% in 45 hrs., the stationary stage being reached in 150 hrs.); after 700 hrs. only 16.8% residue (gel skeleton) remains. The same Me_2CO-extd. crepe, allowed to stand 1.5 yrs., gave a greater quantity (28.1%) of gel skeleton. The sol rubber thus obtained contained 88.18% C and 11.94% H, the gel skeleton 81.35% C, 11.06% H, 2.06% N and 1.02% ash. The latter was allowed to stand 6 weeks under C_6H_6, and the clear C_6H_6 liquid then evapd. *in vacuo*, yielding a gel rubber with 88.23% C, 11.88% H and 0.15% N. To det. whether or not the increase in sol rubber after extn. with Me_2CO was due to the heating rather than the action of the Me_2CO, 1 sample of *raw* crepe was heated 6 days at 60° under CO_2, and another allowed to stand 6 days in Me_2CO, and the 2 samples, together with a 3rd of untreated crepe, were allowed to stand 6 days under Et_2O with occasional shaking. The 1st yielded 82.3, the 2nd 56.7, the 3rd only 40% sol rubber. The increased sol rubber yield is therefore chiefly a thermal effect. After standing a yr. under CO_2 the gel skeleton yielded to Et_2O 4.6% more rubber than calcd. from its extn. curve at the time of its prepn.; after heating 30 days at 60–5° it contained 27.5% sol rubber. (4) With the continuous extn. method the sol rubber in smoked sheet dissolves rapidly in Et_2O; the curve shows a quite marked inflection at 70% extn. after 60–70 hrs.; final value after 700 hrs., 86%; the gel skeleton contains 77.89% C, 10.90% H, 3.26% N, 1.91% ash. *III. Relations between sol and gel rubber.*—These depend on the previous history of the prepn. and can well be explained on the basis of an equil. attainable from both sides, but, as already pointed out (*C. A.* **22**, 4005) not all sol fractions are involved uniformly in the assumed "equil." **VIII. Preparation and molecular size of isorubber nitrone.** Rudolf Pummerer and Wolfgang Gündel. *Ibid* 1591–6.—P. and G. have been studying Bruni and Geiger's isorubber nitrone (I) (*C. A.* **21**, 4092) to see whether it might be used to distinguish between sol and gel rubber and to det. the mol. wt. of the rubber mol. Only PhNO was used. As a whole B. and G.'s observations were confirmed, but with PhNO it is very difficult to prevent a slight absorption of O, especially when, according to B. and G.'s general method, the components are warmed 15 min. in C_6H_6 on the H_2O bath. I, both in soln. and in solid form, is far more sensitive than rubber to O. It is best to work in the cold and in as concd. a soln. as possible in C_6H_6 under CO_2 or

N_2. The originally very viscous soln. becomes mobile in 20–30 min., while the whole reaction requires 1–2 days, depending on the temp., for its completion. In C_6H_6 and $PhNO_2$ the I produces depressions of the f. p. corresponding to a mol. wt. of 1200–1400 (calcd. for a substance formed from a rubber mol. with 8 isoprene groups condensed with 8 mols. PhNO with loss of 16 H atoms, 1384). As in the menthol detns. on rubber, the measurement must be taken only when constancy is reached (1–2 hrs.); after this, the value does not change in 14 hrs. The conclusions previously reached (from the menthol detns.) as to the size of the rubber mol. are thus confirmed. C. A. R.

A new plasticizing agent for rubber. PATSCHKE. *Caoutchouc & gutta-percha* **25,** 14,156–7(1928).—*Caoutchol* is a brown-black oil, with an odor resembling pine tar, and practically non-volatile below 200°. It is a true softener according to the terminology of Burbridge (cf. *C. A* **21,** 1030). It has antioxidant properties, is a mild accelerator, and is useful in reclaiming. C. C. DAVIS

Stress-strain curves for plastic sulfur and raw rubber at various temperatures. JOHN D. STRONG. *J. Phys. Chem.* **32,** 1225–30(1928).—Detns. of the stress-strain curves of raw rubber and of plastic S at various temps., in which the data were recorded automatically and were practically independent of plastic flow, showed that there is a marked similarity between the curves of these 2 substances, the same characteristic inflection point being evident in each case. The *prepn. of plastic S* was carried out by pouring the S into aq. NaCl below 0°, under which conditions it was of a clear yellow color and retained its elastic properties for many hrs. With a means of stabilizing this elasticity, plastic S should be a satisfactory and cheap *substitute for rubber.* C. C. DAVIS

Sulfur and selenium. WEBSTER NORRIS. *India Rubber World* **78,** No. 4, 60–2 (1928).—A description, from the historical point of view, showing the results obtainable with the use of Se in conjunction with S. C. C. DAVIS

Elastic behavior of india rubber. G. B. DEODHAR AND D. S. KOTHARI. *Indian J. Physics* **2,** 305–18(1928); cf. *C. A.* **17,** 1917.—A dynamical method is described for detg. the variation of the modulus of rigidity of rubber with stress. Tests of 3 samples showed that the rigidity increases linearly with stress up to the breaking point. A qual. study of the effects of heat shows that a stretched band, when heated to about 100°, contracts, but if the heating is stopped the band extends until its length exceeds that before heating, and this extension is permanent. It is possible that, just after heating, the rigidity falls considerably, but after some time it regains almost its initial value at that load. The logarithmic decrement, unlike that of a metal, decreases with the load. The behavior of metals is similar, the difference being one of magnitude only. In variation of "torsional stiffness" with load, the behavior of rubber seems to resemble that of annealed wire. B. C. A.

New developments with dispersed rubber. H. A. WINKELMANN. Philadelphia Rubber Works Co. *India Rubber World* **78,** 53–5(1928).—A description of the more recent developments (cf. Tuttle, *C. A.* **17,** 2204; **18,** 1065; **19,** 1207, 1792; Pratt, *C. A.* **18,** 2086; **19,** 420; **20,** 678; **21,** 291, 1568, 3767). Aq. dispersions are finding an increasing no. of uses outside of the rubber industry, notable among which are in the textile and paper industries. Thus in the *textile industry,* aq. dispersions can be used in the manuf. of automobile topping, rugs, mats, upholstery, raincoats, bags and webbing. In the *paper industry,* pulp may be impregnated with dispersed rubber, besides which it is used in the manuf. of bags and wall board. Other newly developed uses, some in an exptl. stage, are described. The technic of the prepn. of aq. dispersions has been improved, including the use of a variety of *dispersing agents* to suit best the particular problem, such as fatty acids, soaps, glues, saponins, sea moss, albumins and clays. The types of rubber, or rubber mixts. which it is possible to disperse are practically unlimited, and uniform consistency, concn. and quality are readily secured. C. C. DAVIS

Dispersion of pigments in rubber. I. Microscopical studies of agglomeration and flocculation. ERNEST A. GRENQUIST. Fisk Rubber Co. *Ind. Eng. Chem.* **20,** 1073–8(1928).—The tendency during milling of particles to pack and form secondary units is defined as *"agglomeration,"* and dense formations of completely dispersed particles originating during vulcanization as *"flocculation."* *"Aggregation"* refers to cases where agglomeration and flocculation cannot be distinguished. A review of the literature (63 references to which are given) deals with the various factors which govern the dispersion of pigments in rubber, especially agglomeration and flocculation. Expts. are then described in which various pigments, including S, C black, ZnO, stearic acid, di-*o*-tolylguanidine in various combinations, were mixed in rubber and their state of dispersion, agglomeration and flocculation were detd. microscopically. In many cases the behavior was similar to dispersed particles in other systems. Agglomeration occurs around larger foreign nuclei. During vulcanization or even during heating of

a rubber-C black mixt., flocculation of previously dispersed particles occurs, the causes and effects of which seem to vary with the components and the conditions.
C. C. DAVIS

Organic rubber colors. W. J. S. NAUNTON. *Trans. Inst. Rubber Industry* **4**, 68–84(1928).—A crit. review and discussion of present developments in the use of org. colors in rubber, with certain new data. Tests of the aging effects of some typical org. colors compared with red Fe oxide and ultramarine showed that, in general, org. colors do not have a deleterious effect on natural aging, but may hasten deterioration when the rubber mixts. are heated in air at 70°, unless protected by an antioxidant. The problems encountered in the use of org. colors in latex to be vulcanized or electrolyzed and in dry rubber mixts. are then discussed. Colors can conveniently be divided into those (1) sol. in rubber; (2) slightly sol. in rubber, and (3) insol. in rubber, the latter class including org. pigments and lakes. Sol. colors must not be used in proportions above the soly. limit; otherwise they crystallize out (bloom). At ordinary temp. this limit is about 0.3% in pale crepe. Some substances (*e. g.*, Fe oxide) promote this crystn. and blooming; others inhibit it. Incorporation of colors in rubber may be facilitated and made more nearly uniform by converting the colors to their stearates by preliminary fusion with stearic acid. Colors slightly sol. in rubber have certain advantages which make them the most satisfactory class. In making transparent rubber, Zn and Cd stearates are the best activators, Cd stearate being preferable in most cases. Various troubles are also encountered in the manuf. of various colored ebonites, which may be minimized by the proper combination of S, accelerator, choice of color and conditions of curing. A general discussion follows the paper. Also in *Rubber Age* (*London*) **9**, 254–61(1928).
C. C. DAVIS

Carbon blacks and their use in rubber. III. Aging effects. L. B. COX AND C. R. PARK. Delano Land Co., Los Angeles. *Ind. Eng. Chem.* **20**, 1088–91(1928).—In continuation of the earlier expts. (cf. Goodwin and Park, *C. A.* **22**, 3802) the influence of the various blacks on the aging of rubber mixts. contg. the blacks was studied. Changes in the tensile strength and resistance to abrasion and increases in wt. were used as criteria of the aging. The aging varied with the different blacks, the best aging being obtained with Thermatomic, followed by Goodwin, Charlton, Micronex and Super Spectra in the order named. With respect to the influence of accelerators on the aging, the beneficial influence increased in the order: diphenylguanidine, hexamethylenetetramine, ethylideneaniline, mercaptobenzothiazole. Stearic acid showed no influence on the aging properties of the vulcanizates.
C. C. DAVIS

Critical discussion of results of tests of carbon black mixings with reference to hysteresis losses and the relation of these tests to the resistance to deterioration. LOTHAR HOCK. *Kautschuk* **1928**, 89–90.—Tests, based on an earlier publication by H. (cf. *Kautschuk* Sept. **1925**), are described, in which the influence of "Durex" C blacks in an accelerated rubber mixt. was detd.
C. C. DAVIS

Critical discussion of tests of carbon black mixings. WERNER ESCH. *Kautschuk* **1928**, 115–6.—Comments on a paper by Hock (cf. preceding abstr.)
C. C. DAVIS

Recording roll heat of calenders. C. E. MAYNARD. Fisk Rubber Co. *India Rubber World* **78**, 62(1928).—A new *automatic app.* is described and illustrated.
C. C. DAVIS

Reënforcement of rubber by fillers. JOHN T. BLAKE. Simplex Wire & Cable Co., Cambridge, Mass. *Ind. Eng. Chem.* **20**, 1084–8(1928).—A new *theory of the reënforcement of rubber by pigments* is advanced, in connection with which a reënforcing filler is considered to be one which forms a bond with the rubber which is stronger than the matrix itself. The ΔA function of Wiegand (cf. *C. A.* **19**, 3386) is a practical means of expressing the reënforcing effect of a filler, but the range of vol. over which the bonding of the filler is greater than the strength of the rubber matrix gives a better understanding of the condition of the filler in the rubber. A *"mol. tensile" curve* serves to illustrate and substantiate this point of view. The *mechanism of the dispersion of fillers or pigments* is then studied theoretically, the work of Langmuir and Harkins being adapted to show that the fatty acids and esters are responsible for the wetting and dispersion of the particles. Calcns. of the quantity of these dispersing agents and of the heats of wetting conform to the exptl. values. In this way the *role of fatty acids and other polar compds.* is put on a sound theoretical basis. Rubber mixts. may be improved by delaying the break in the mol. tensile curve by increasing the range over which dispersion is complete.
C. C. DAVIS

Balata gum. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **25**, 14,111–5, 14,154–6(1928); cf. *C. A.* **22**, 4005.—A general treatise on the characteristics and uses.
C. C. DAVIS

The aging of rubber. Its preservation. F. JACOBS. *Caoutchouc & gutta-percha* **25**, 14,110–1(1928); cf. *C. A.* **22**, 1057, 4004.—Some of the most recent aging tests, such

as the Marzetti O test (cf. *C. A.* **17**, 2975), the aging wheel of the Office des Inventions (cf. *C. A.* **21**, 1899) and the Hanau analytical lamp (cf. Krahl, *C. A.* **21**, 2816), are described. C. C. DAVIS

Changes in composition of rubber on aging. M. SAGAJLO. *Przemysl Chem.* **12**, 184–90(1928).—Analyses of several rubber mixts. showed that on aging not only the acetone-sol. content but also the $CHCl_3$-sol. content and substances saponifiable in alc. KOH increase in the rubber. A. C. ZACHLIN

Laboratory devices for studying the aging and vulcanization of rubber. R. FRIC. *Chimie et industrie* Special No., 547–8(April, 1928).—A detailed description of a pressure oven for carrying out artificial aging tests in air or O_2 under pressure, as suggested by Bierer and Davis. Heating is obtained by induced currents. A. P.-C.

American vulcanization accelerators. RUDOLF DITMAR. *Chem.-Ztg.* **52**, 730 (1928).—The characteristics of the Am. accelerators termed in the trade *A*-11, *A*-16, *A*-19, *A*-20, *A*-50 and *Z*-88 are described briefly, including their fluorescent colors in ultra-violet light. C. C. DAVIS

A scheme for accelerator classification. R. P. DINSMORE AND W. W. VOGT. Goodyear Tire & Rubber Co. *Rubber Age* (N. Y.) **23**, 554–7(1928).—See *C. A.* **22**, 4273. C. C. DAVIS

The microscopy of the vulcanization of rubber. ERNST A. HAUSER AND M. HÜNEMÖRDER. *Caoutchouc & gutta-percha* **25**, 14,146–9(1928). (Accompanying illustrations on sep. sheet.)—An *app.* is described, with which it is possible to observe continuously the changes which rubber mixts. undergo when heated. In 1 modification of the app., tiny samples are heated directly in steam, in another modification they are heated under compression indirectly by steam, in each case steam under known pressure being passed through or around the chamber contg. the sample, the latter being under observation through a microscope. By this means it was possible to observe the *behavior of S during vulcanization.* At a pressure of 3 atms., the S fused, the total mass became semi-fluid and the droplets of S dissolved in the rubber without any intermediate phase (cf. Dannenberg, *C. A.* **21**, 835, 3764). The mass then remained optically empty, but soon after the heating was stopped, droplets of S appeared in continuously increasing no. These droplets then migrated to form chains. The longer the heating the less was this tendency for S to sep. and form chains. With accelerators present, fusion of S began sooner, general softening of the mass was less, and instead of droplets forming chains, the S sepd. directly on the surface in rhombic form. The same general phenomena took place with ZnO, though softening and subsequent sepn. of S were less pronounced. Colloidal ZnO behaved somewhat similarly to S, dissolving during vulcanization and sepg. again later. The app. is applicable to the study of the *behavior of compounding ingredients in general.* A review of earlier attempts to observe change during vulcanization is included. C. C. DAVIS

Watch-case vulcanizers. JOSEPH ROSSMAN. *India Rubber World* **78**, No. 4, 67–9 (1928); cf. *C. A.* **22**, 4273.—A description, from the historical point of view, of the development of this equipment. C. C. DAVIS

Measurement of the tread movement of pneumatic tires and a discussion of the probable relation to tread wear. W. L. HOLT AND C. M. COOK. *Bur. Standards J. Res.* **1**, 19–28(1928).—*Lab. abrasion tests* to simulate road wear should use a non-linear abrasive movement since most of the tread surface is abraded by curved motion. C. C. DAVIS

Patents

Rubber. HAROLD E. CUDE (to Naugatuck Chemical Co.). U. S. 1,680,862, Aug. 14. Comminuted rubber is treated with oleic or stearic acid or other org. acid capable of forming a water-sol. soap, until the mass has assumed a putty-like consistency, and residual acidity is neutralized with a base such as NaOH capable of forming a water-sol. soap. The product may be dispersed in aq. liquids.

Rubber. TECHNISCHE CHEMIKALIEN-COMPAGNIE G.M.B.H. Fr. 633,794, May 3, 1927. Rubber is treated before vulcanization with mineral oils contg. unsatd. compds. of S and OH and is characterized by the fact that the oils are activated by heating to 135–150° and drying.

Treating rubber latex. W. A. GIBBONS (to Naugatuck Chemical Co.). Brit. 282,011, Dec. 9, 1926. Concd. latex contg. alkali preservative is neutralized or slightly "overneutralized" to improve its plasticity and cohesiveness on the mixing mill or other app. H_3PO_4 or HOAc or a buffer material or salt which hydrolyzes to give an acid reaction such as primary Na phosphate or Zn acetate may be used.

Treating rubber latex. SIDNEY M. CADWELL (to Naugatuck Chemical Co.). U. S. 1,680,856, Aug. 14. In making various rubber articles, a rubber dispersion is treated with a metallic compd. such as ZnO and with NaOAc or other suitable org. acid salt capable of reacting to liberate metallic ions in the dispersion to form an uncoagulated compn. of increased filterability, and rubber is deposited from the latex thus obtained directly on a porous form in the shape of the desired article. U. S. 1,680,857 specifies prepg. a vulcanized latex by adding, to an approx. NH_3-free latex contg. sufficient non-nitrogenous CS_2 accelerator, ZnO and S to cause the latex to be vulcanized to a soft elastic product, and then sufficient addnl. S, ZnO and tetramethylthiuramdisulfide to cause the rubber to be vulcanizable to a hard rubber at temps. below 100°. U. S. 1,680,858 specifies forming rubber articles from latex by vulcanizing the latex in the presence of a salt of a thiol acid such as Na dithiobenzoate and depositing the latex directly on a porous form.

Warming mill and associated apparatus for treating rubber stock. OSCAR D. HOLLENBECK. U. S. 1,680,171, Aug. 7.

Mold for rubber airbags, etc. LEON S. WASHBURN (to The Goodyear Tire & Rubber Co.). U. S. 1,679,554, Aug. 7. Structural features.

Apparatus for making seamless rubber tubing. CHARLES H. ROTH (to The Goodyear Tire & Rubber Co.). U. S. 1,679,545, Aug. 7.

Abrasion testing machine for testing rubber tire treads, etc. DUNLOP RUBBER CO., LTD., and L. J. LAMBOURN. Brit. 282,131, Sept. 1, 1926.

Coating metals with rubber. FRITZ AHRENS. Fr. 634,128, May 10, 1927. In coating metals with a soln. of rubber, the product obtained by treating oxidizable oils with sulfur chloride is added to the soln.

Rubberized fabric driving belts. C. MACINTOSH & Co., S. A. BRAZIER and T. E. ANDREW. Brit. 282,271, May 6, 1927. Driving belts, bands, ropes or the like such as those for use in textile machinery are immersed in a natural or artificial rubber dispersion, which may contain added compounding or vulcanizing ingredients, dried and vulcanized. The material may be preliminarily treated with dil. NH_3 soln. to render it more permeable, and may be alternately dipped in the rubber dispersion, and dried between dippings, to obtain any desired degree of rubberization. Vulcanization may be effected by steam or dry heat.

Rubber-composition flooring. JOHN B. LOSEY and WALTER R. STONE. U. S. 1,678,948, July 31. Structural features are specified of a material comprising a base of relatively soft rubber compn. and surface sections of harder rubber compn.

Treating waste material containing rubber and fiber. REED P. ROSE (to Mechanical Rubber Co.). U. S. 1,680,915, Aug. 14. Tire casings or similar waste material is disintegrated and worked mechanically with about 10% its quantity of a soap-forming fatty acid such as oleic or stearic acid until a mixt. of plastic, putty-like consistency is produced; NaOH in quantity 1.2–1.5 times that of the added fatty acid is then added, and the material is further worked and then beaten in an aq. medium contg. an alkali such as NaOH together with glue, casein or other protective colloid, until the rubber is completely removed from the fiber and in dispersed form.

Composition for softening and use as a filler in making vulcanized rubber mixtures. CLAYTON O. NORTH (to The Rubber Service Laboratories Co.). U. S. 1,679,000, July 31. A mineral lubricating oil of a viscosity of not over 120 sec. Saybolt at 38° is mixed with a small proportion of cotton seed oil.

Vulcanizing rubber. LORIN B. SEBRELL (to The Goodyear Tire & Rubber Co.). U. S. 1,679,548, Aug. 7. Vulcanization is accelerated by the use of mercaptoaminobenzothiazole or other mercaptoarylthiazole, the aryl structure of which contains an amino group. Cf. *C. A.* **22**, 2686.

Vulcanizing rubber coverings of rollers or other hollow articles. C. H. GRAY. Brit. 282,502, Sept. 24, 1926. Mech. features.

Plastic material from latex and asbestos. WILLIAM B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,680,234, Aug. 7. A product suitable for *insulating wire* is made by washing asbestos with acid and mixing it with latex.

Rubber. L. C. PETERSON. Brit. 283,122, Jan. 3, 1927. In the manuf. of sheet material with layers of vulcanized and unvulcanized rubber, the unvulcanized layer has incorporated in it a neutralizer of vulcanizing agents such as small quantities of HCl, H_2SO_4 or H_3PO_4 to prevent partial vulcanization of this layer due to migration of the vulcanizing agents. Examples and formulas are given. Cf. *C. A.* **21**, 3490.

Rubber. TOKYO GOMU KABUSHIKI KAISHA. Fr. 634,628, May 18, 1927. A rubber which will float on water and is resistant to oils is made by mixing factis, S, alkali soap and diphenylguanidine with the crude rubber instead of the usual mineral solids.

Porous rubber. FERDINAND RINGER. Fr. 634,694, May 19, 1927. Metallic

carbonates or bicarbonates are added to rubber before vulcanization so that the liberation of gas during vulcanization causes a swelling of the rubber.

Rubber solutions. J. Y. JOHNSON. Brit. 282,618, June 10, 1926. In prepg. rubber solns. which also may contain nitrocellulose, coloring substances, etc., there is used as solvent the oily product obtained by the catalytic hydrogenation of oxides of C by processes such as described in Brit. 227,147 (*C. A.* **19**, 2673), Brit. 229,714 (*C. A.* **19**, 3093), Brit. 237,030 (*C. A.* **20**, 1414) and Brit. 238,319 (*C. A.* **20**, 1995) or a fraction of such a product or the product of hydrogenation, esterification or condensation of such products or fractions. Solns. suitable for use as lacquers may be thus prepd.

Isomerizing rubber. H. L. FISHER (to B. F. Goodrich Co.). Brit. 282,778, Dec. 28, 1926. Thermoplastic products are obtained by heating rubber with a phenol and a third substance which may be chlorinated rubber, rubber hydrochloride, rubber S chloride, chlorinated rubber hydrochloride, pinene hydrochloride, diphenylamine hydrochloride, trichloroaniline hydrochloride, *m*-nitroaniline hydrochloride, $HgCl_2$, $SnCl_4$, naphthalene tetrachloride, triphenyl chloromethane, $ZnBr_2$, rubber dibromide, diphenylamine hydrobromide, $CaSO_4$, $Al_2(SO_4)_3$, $HgSO_4$, diphenylamine sulfate or diphenylamine trichloroacetate. The materials may be heated for 20 hrs. at 134–160°.

Coating metals with rubber. R. M. WITHYCOMBE. Brit. 282,737, Dec. 30, 1926. A soln. of rubber contg. S is applied to metal surfaces, the solvent is allowed to evap., and the surface is subjected to dry heated air (suitably at a temp. of about 110–130°). The soln. may also contain oxides, pigments and accelerators.

Direct production of rubber goods from rubber dispersions. PAUL KLEIN and ALBERT HEALEY (to American Anode Incorporated). U. S. 1,683,588, Sept. 4. The degree of coagulation is regulated by adding soft soap to natural latex in the proportion of 6–12 g. soft soap to 1 l. of latex and the latex is deposited by electrophoresis upon an anodic mold.

Curing rubber tubes upon a mandrel. DANIEL E. HENNESY (to Fisk Rubber Co.). U. S. 1,682,124, Aug. 28. A film of cement is interposed between the ends of the tube and the mandrel during vulcanization, to avoid need of binding to prevent blowing. U. S. 1,682,125 specifies heating the end portions of the tube to soften the rubber preparatory to vulcanization, and clamping the end portions to the mandrel.

Composition for filling tires. A. E. MILLS and W. T. GALBRAITH. Brit. 283,249, Sept. 25, 1926. A compn. formed of ground burnt cork 5, glue 3.5, linseed and castor oil 1, rubber latex 0.5 and "cellulose derivs." 0.25 part is mixed with 2–4% NaOH, about 2% oxide of Mn or Pb or $ZnCl_2$ and 2% of chrome alum, and steam is blown through the materials for 5–10 hrs. Turpentine 2% is added and heated air is passed through the mass for 4–12 days after which it is rolled and molded.

Rubber flooring material. CHAUNCEY C. LOOMIS (to Latex Products, Inc.). U. S. 1,682,530, Aug. 28. A flooring comprises a dried non-vulcanized rubber latex and asbestos, clay, wood, cork or other suitable filler; a large proportion of the rubber content may be adjacent the upper surface of the material.

Accelerators for rubber vulcanization. L. B. SEBRELL and J. TEPPEMA. Brit. 282,947, Nov. 9, 1926. Mercaptothiazoles are made by reducing *o*-nitrohalogenaryl compds. with a sol. basic hydrosulfide in the presence of CS_2 and H_2S; *e. g.*, 2-mercaptobenzothiazole is made by suspending *o*-nitrochlorobenzene in an aq. soln. of Na sulfide satd. with H_2S, warming and passing H_2S and CS_2 through the mixt.

Accelerators for rubber vulcanization. WM. P. TER HORST (to Rubber Service Laboratories Co.). U. S. 1,682,728, Aug. 28. The reaction product of piperidinepentamethylene dithiocarbamate with dithiazyl trithiocarbonate or a similar compd. is used as an accelerator. U. S. 1,682,729 specifies the use of the reaction product of piperidine with dithiazyltrithiocarbonate or similar products.

Substituted thiuram polysulfides. GEORGE S. WHITBY (to Roessler & Hasslacher Chemical Co.). U. S. 1,681,717, Aug. 21. The products formed by treating the salts of substituted dithiocarbamic acids with S_2Cl_2 or SCl_2 may be used as *accelerators in the vulcanization of rubber*. Examples are given of the prepn. of diphenylethylthiuram tetrasulfide, diphenylethylthiuram trisulfide and diphenylmethylthiuram tetrasulfide, which may be formed from the corresponding Na or NH_4 phenylalkyldithiocarbamates.

Vulcanizing rubber. RALPH V. HEUSER (to Albert C. Burrage, Jr.). U. S. 1,681,806, Aug. 21. An *o*-tolylguanidine such as tritolylguanidine is used as an accelerator. Cf. *C. A.* **22**, 2856, 3318.

Vulcanizing rubber. I. G. FARBENIND. A.-G. Brit. 282,892, Sept. 30, 1926. Formamide is used as an accelerator.

Compounds resembling rubber. I. G. FARBENIND. A.-G. Fr. 634,857, May 23, 1927. The products coming from the hydrogenation under pressure of mineral oils, coal and other carboniferous substances are dehydrogenated and (or) dissocd. to give unsatd. compds. and then polymerized. The polymerization may be replaced by a

fixation on the compds. of other elements or compds. such as halogens, hydrohalogen acids, hypohalogenous acids or HCN. The dehydrogenation or the dissocn. may be accomplished in several steps.

Vulcanized rubber compositions. PHILIP SCHIDROWITZ (to Vultex Ltd.). U. S. 1,682,857, Sept. 4. Vulcanization of compns. contg. uncoagulated rubber is effected, *e. g.*, by use of Na polysulfide and an accelerator, at a temp. below the temps. ordinarily employed in hot vulcanizing methods and under such conditions as to prevent any substantial coagulation of the rubber during the vulcanization.

Rubber. WILLIS A. BOUGHTON. Can. 283,464, Sept. 25, 1928. A soln. of ammonium polysulfide is made to react with latex, the liquid is evapd. and the residue heated and vulcanized.

Rubber composition. CHARLES H. CAMPBELL (to American Glue Co.). U. S. 1,683,862, Sept. 11. Sol. and diffusible cleavage products obtained by the hydrolytic decompn. of collagen (short of amino acids) are mixed with rubber. U. S. 1,683,863 specifies the use of products similarly obtained from keratin and U. S. 1,683,864 relates to similar compns. also contg. glue.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 283,840, Jan. 14, 1927. Hydrocarbons suitable for manuf. of synthetic rubber such as butadiene, isoprene and dimethylbutadiene are emulsified (*e. g.*, with water and soap and egg albumin or with Na isobutylnaphthalenesulfonate) and then polymerized in the presence of O or substances such as a perborate or percarbonate which yield O.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 283,841, Jan. 15, 1927. Polymerization of hydrocarbons such as butadiene, isoprene or dimethylbutadiene is effected by treatment with an alkali metal such as Na or K, in an atm. of H, N or CO_2 and in the presence of an org. hydroxy compd. or ether of high mol. wt. such as glycerol, starch, cellulose, a cellulose ether or superficially oxidized rubber. Temps. of 40–60° are suitable for effecting the polymerization in various examples which are given.

Rubber from sprayed latex. DUNLOP RUBBER CO., LTD., AND D. F. TWISS. Brit. 283,984, Sept. 17, 1926. Latex or a similar aq. rubber dispersion (which may be mixed with various modifying agents) is sprayed in a damp unheated state upon the unheated surface of a mold or former.

Solvent and dispersing agents for rubber. EBERHARD MEYER. Ger. 463,290, July 5, 1928. Esters of tetrahydronaphthol, *e. g.*, tetrahydronaphthol acetate or naphthenate, are used as non-volatile solvents or dispersing agents for rubber.

Making laminated rubber tire tubes from sheet material. ALBERT E. HENDERSON. U. S. 1,683,669, Sept. 11. Mech. features.

Coating metals with rubber. F. AHRENS. Brit. 283,049, April 16, 1927. Rubber coatings are attached to metals by use of a rubber soln. contg. S chloride or other suitable acid substance which attacks the metal and facilitates the formation of metal sulfide which assists in bonding of the metal and rubber. Oils such as a mixt. of rape and linseed oils also may be added to the rubber soln. Cf. *C. A.* **22**, 3806.

Porous rubber. H. ZIEGNER. Brit. 283,566, Jan. 14, 1927. A porous material such as wood sawdust is first satd. with a swelling medium such as benzine and then mixed with rubber compns. which may also contain fillers and vulcanizing reagents. The benzine or the like first causes the rubber to swell where it contacts with the added porous material and then during the drying operation to contract and become loosened from the sawdust or other added particles. The porosity may be further increased by adding water, which evaporates during vulcanization and enlarges the pores.

Rubber articles. ANODE RUBBER CO., LTD. Brit. 283,871, Jan. 18, 1927. The properties of articles made directly from rubber latex (suitably by electrophoresis or dipping) are modified by adding to the latex an artificially prepd. dispersion of coagulated rubber, gutta, balata or similar material. Various coloring, vulcanizing and modifying agents may also be added.

Rubber articles. DOUGLAS F. TWISS (to The Dunlop Rubber Co., Ltd.). Can. 283,262, Sept. 11, 1928. Articles of rubber are manufd. by treating the surface of a mold with a layer of jelly including a coagulant of the character of Na_2SiF_6, and dipping the mold into the material of which the article is to be formed.

Rubber heels. RICHARD F. KINSLEY (to Dryden Rubber Co.). U. S. 1,684,100, Sept. 11. In forming heels from ground waste vulcanized rubber, partially cured blanks of smaller area but greater thickness than the finished article are inserted in a mold, a layer of rubber material of greater plasticity and lesser elasticity than that of the blank is placed on the latter and the assembly is subjected to heat and pressure.

Vulcanization accelerator. W. J. KELLY. Brit. 283,679, Nov. 9, 1926. 1-Mercaptobenzothiazole, used as an accelerator, is made by heating to about 280° in an autoclave, $PhNH_2$, S and CS_2. The product is dissolved with NaOH and pptd. with HCl.

Vulcanization accelerator. L. B. SEBRELL. Brit. 283,661, Oct. 26, 1926. 1-Mercaptobenzothiazole, used as an accelerator, is made by heating under pressure a mixt. of NH_3 (as gas or aq. soln.), CS_2, $PhNH_2$ and S.

Latex composition. WILLIS ALEXANDER GIBBONS (to The Dominion Rubber Co., Ltd.). Can. 282,491, Aug. 14, 1928. Natural latex is concd. to a compn. contg. over 50% solids and preserved with ammonia, H_3PO_4 is added to neutralize the alkali, without coagulating the rubber content of the latex, the water is evapd., and all the solids contained in the latex are recovered. Cf. *C. A.* **22**, 3805.

Treating rubber latex. SOCIETÀ ITALIANA PIRELLI and U. PESTALOZZA. Brit. 284,608, Jan. 31, 1927. Latex is treated at a low temp. by adding small quantities of substances such as solns. or suspensions of salts of bi- or ter-valent metals, and is then heated to effect coagulation or thickening; *e. g.*, 0.15% of a slightly sol. Ca salt and 0.1% of ZnO suspended in "ammoniacal water," may be added to ammonia-preserved latex contg. 50% of rubber. At temps. of 20° or lower no coagulation occurs but on heating to 95–97° rapid coagulation is effected. Fillers, vulcanizing agents, etc., may be added and the process may be applied to the manuf. of molded articles, extruded tubes, etc.

Jelutong product. SHELDON S. YATES (to Chicle Development Co.). U. S. 1,685,797, Oct. 2. Jelutong latex is coagulated and the coagulant is melted and water is expelled to reduce the water content below 5%; the melted mass is then poured into molds and permitted to cool and is suitable for transportation and storage. Cf. *C. A.* **22**, 1705.

Electrodeposition of rubber, etc. DUNLOP RUBBER CO., LTD., P. KLEIN and A. HEALEY. Brit. 284,736, Aug. 4, 1926. The toughness of deposits of rubber, gutta-percha and the like produced from dispersions is increased by incorporating with the aq. dispersions peptizing agents such as protective colloids, *e. g.*, soft soap, in excess of the quantities normally employed for protective purposes. Soft soap 6–12 g. may be used with each l. of latex contg. 30% rubber.

Rubber emulsions. J. M. A. TOUCHON. Brit. 284,244, Jan. 25, 1927. Rubber emulsions which may be used as substitutes for natural latex are prepd. by passing a thick rubber soln. together with water contg. an emulsifying agent through a high-speed emulsifying app. and removing the rubber solvent from the emulsified product by low-temp. distn. Numerous details are given.

Rubber compositions. E. YOSHIOKA. Brit. 284,912, May 19, 1927. A "buoyant rubber" for oil hose contains factis up to 3%, S 5%, an alk. soap insol. in mineral oils and melting at the vulcanizing temp. 1%, diphenylguanidine 1% and rubber over 80%.

Regeneration of rubber. WALDEMAR SCHEITLAUER. Can. 283,709, Oct. 2, 1928. Ground waste rubber is regenerated by mixing with a NaOH soln. which has been in contact with cellulosic substances as used and discharged as a waste product in the production of viscose, and treating the mixt. in autoclaves in the usual way.

Spongy rubber. R. J. NOAR. Brit. 284,938, July 19, 1927. In manuf. of sponge-rubber articles, a vulcanized skin is formed on the surface of a mass of dough before gas is generated in the mass and the whole mass is then hot vulcanized. To effect the superficial vulcanization and skin formation a cold process may be used or there may be employed a "super-accelerator" such as piperidine piperidyl dithiocarbamate or tetramethyl-thiuram disulfide at a temp. below that at which gas is generated. Various details are given.

Surface layer of sponge rubber on rubber goods. SATARO MORIMOTO. U. S. 1,685,954, Oct. 2. A soln. of unvulcanized rubber mixed with materials such as $(NH_4)_2CO_3$, S and fillers which convert ordinary rubber into spongy rubber is applied to the surface of unvulcanized rubber goods and the assembly is then cured by a hot process.

Products of rubber with metallic salts. H. A. BRUSON (to Goodyear Tire & Rubber Co.). Brit. 285,071, Feb. 11, 1927; Can. 283,757, Oct. 2, 1928. Rubber is treated with metallic salts such as $SbCl_5$, $SnCl_4$, $TiCl_4$, $FeCl_3$, or BCl_3, to form addn. products which contain a plurality of hydrocarbon mols. linked together and from which the metal salt may be split off to obtain a product thought to be a polymer of rubber. Both the addn. product and the polymer absorb O from the air.

Rubber-surfaced roads, floors, etc. J. J. HORNE and C. F. HENDRICK. Brit. 285,203, Dec. 18, 1926. Structural features.

Ornamenting rubber articles. DUNLOP RUBBER CO., LTD., and G. W. TROBRIDGE. Brit. 285,113, Oct. 14, 1926. Bathing caps or other rubber articles formed by electrophoretic deposition are treated in a press with heated embossed, engraved or stamped plates during or prior to vulcanization.

Apparatus for making rubberized cord sheet material. JOHN W. CLARK. U. S. 1,686,436, Oct. 2.

Sulfurized oil compositions. A. DE WAELE. Brit. 284,415, Nov. 3, 1926. Vul-

canized oil compns. are made by treating with S chloride, S thiocyanate, dithiocyanogen (or similar vulcanizing agent reacting energetically with glycerides of hydroxy unsatd. fatty acids) an ester of an unsatd. higher fatty acid in which one of the H atoms of the fatty acid residue is substituted by an electronegative atom or group which is less electronegative than the OH group, *e. g.*, Cl or the acetyl, formyl or carbonate group, *e. g.*, acetylated castor oil or acetylated oxidized or blown oils. Fillers and other substances may also be added.

Tightening means for re-rubbering or molding pneumatic tires. MICHEL LAMOUROUX. Fr. 635,944, June 14, 1927.

Vulcanizing rubber. LORIN B. SEBRELL (to The Goodyear Tire and Rubber Co.). Can. 282,883, Aug. 28, 1928. A mixt. of rubber, a vulcanizing agent and a zinc salt of 1-mercapto-3,5-dimethylbenzothiazole is heated. Cf. *C. A.* **22**, 3806.

Vulcanized rubber. VULTEX, LTD. Ger. 462,858, June 28, 1928. Addn. to Ger. 391,635. Previously concd. latex of over 55% concn., preferably 60–70%, is vulcanized with the usual fillers, accelerators, etc.

Hot vulcanization of rubber. B. V. BUIZOV. Russ. 3831, Oct. 31, 1927. Alkali salts of trithiocarbonic acid are added to a mixt. of rubber, S and the customary ingredients in a rubber mass. The mixt. is then vulcanized as usual.

Hot vulcanization of a rubber mixture. B. V. BUIZOV. Russ. 3832, Oct. 31, 1927. Complex NH_3 salts of Ni, Cr, Cu and Co are added to a mixt. of rubber, ZnO, coloring compds. and fillers. This mixt. is vulcanized hot as usual.

Treating waste vulcanized rubber. DUNLOP RUBBER CO., LTD., D. F. TWISS and F. THOMAS. Brit. 284,829, Dec. 20, 1926. Comminuted scrap is admixed with S and with an "anti-ager" such as quinol, aminophenol aldol α-naphthylamine or other condensation product of the aldehydes and aromatic amines (suitably 1% each of the S and "anti-ager") and then subjected to heat and pressure (suitably in a "daylight press" for 30 min. at 150°).

Apparatus for molding and vulcanizing small rubber articles. DUNLOP RUBBER CO., LTD., H. WILLSHAW and T. NORCROSS. Brit. 285,103, Oct. 7, 1926.

Molding and vulcanizing tires. J. R. GAMMETER (to B. F. Goodrich Co.). Brit. 285,359, Feb. 14, 1927. A plastic mixt. which may be formed of clay 100, water 40–50, and waterglass 1–2 parts is used for distending tires before vulcanization. An app. and various mech. details are described.

Apparatus for vulcanization of rubber. THE LIVERPOOL RUBBER COMPANY. Fr. 636,067, June 16, 1927.

Leather substitute. GOVERNMENT RUBBER TRUST "REZINOTREST." Russ. 4159, Sept. 15, 1924. Known accelerators of vulcanization, such as aliphatic hydroaromatic or heterocyclic amines or their salts or derivs. of dithiocarbamic acid, are added to a finely divided mixt. of rubber and leather, sulfur and oxides of the metals Ca, Mg, Zn, Pb, etc. This mixture is heated for the purpose of vulcanization at not over 110°.

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The Effect of Temperature on the Stress-Strain Properties of Vulcanized Rubber[1]

A. A. Somerville and W. H. Cope[2]

Preface

IT has become quite generally recognized by rubber technologists that the physical tests on vulcanized rubber are affected by the temperature of the testing room. It has also been recognized that a tire in service may become quite hot and that the wearing qualities of a tire differ from summer to winter or from hot to cold weather. The existence of the above conditions is sufficient, if any reason is needed, to warrant further laboratory work to learn more about the influence of temperature on the physical properties of vulcanized rubber.

Previous Work

Recently there have been issued at least two published reports showing in considerable detail the results of work along the line of testing rubber at different temperatures. One of these reports by Van Rossem and Van der Meijden on the influence of high temperature on the stress-strain curve of vulcanized rubber, covering work done at the Netherland Government Rubber Institute at Delft, gives results and draws conclusions of tests made at a range of temperatures from 70° to 147° C. on a compound consisting of 92½ per cent of rubber and 7½ per cent of sulphur.

The U. S. Bureau of Standards has published Technological Paper No. 364 showing physical tests obtained on six rubber compounds tested at temperatures varying from —70° to +147° C. The Physical Testing Committee of the Rubber Division of the American Chemical Society has made tests to determine the influence of different temperatures on the tensile, elongation and stress-strain of five compounds and is now engaged in making tests to determine the effect of temperatures ranging from 15° to 35° C. on the abrasive resistance or wearing qualities of four compounds.

In 1925 the Physical Testing Committee of the Rubber Division of the A. C. S. in its report included stress-strain figures supplied by Dinsmore on a compound tested at four different temperatures ranging from 21° to 30°C. Various brief notes about the effect of temperature on the physical tests on rubber have also been made in earlier publications.

Present Work

Due chiefly to interest aroused by reading Bureau of Standards Technological Paper No. 364, wherein results were given showing the effect of various temperatures on what might be termed com-

[1]Presented before the Rubber Division, A. C. S., at the 76th Meeting, Swampscott, Mass., Sept. 10-14, 1928. Courtesy of *Ind. & Eng. Chem.*

[2]R. T. Vanderbilt Co., Inc., New York.

mercial compounds, the authors had a desire to obtain further information along these lines and to this end conceived the idea of a simple method of making fairly accurate tests at different temperatures on vulcanized rubber.

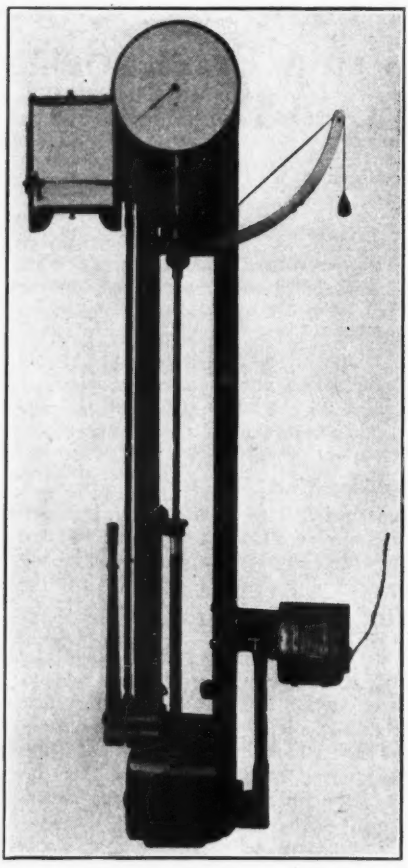


Fig. 1

Method of Test

The method used is quite comparable to the usual methods of testing rubber, but with the additional advantage that the rubber test piece may be subjected to a predetermined fixed temperature while undergoing the test. For this purpose a tank capable of holding liquid is attached to a standard vertical rubber testing machine in such way that the jaws holding the test piece and the test piece itself are submerged in the liquid while the test piece is being stretched, and the stress-strain curve is automatically recorded on the testing machine chart.

Testing Apparatus

Figure 1 shows such a testing machine with hand devices for measuring elongation removed and equipped with jaws for use in testing a ring-shaped sample.

Figure 2 shows the same machine equipped with a tank to hold liquid in which the rubber test piece may be stretched and maintained at the same temperature during the test as the temperature of the liquid.

The tank is a rectangular sheet iron box about 24 inches high mounted on the frame of the testing machine. The stretching bar, motor driven, pulling the lower jaw to which the test piece is attached passes through the bottom of the tank. That part of the stretching bar is a round metal rod and by means of an ordinary packing gland in the bottom, the tank is made practically leak-proof. The tank is provided with long vertical glass windows in front and rear to permit observation of the sample during the test, although this observation is quite unnecessary.

At the bottom of the tank electric immersion heaters are inserted for heating the liquid in the tank. The liquid used in these experi-

ments was water because it could easily be held at the temperatures desired for these tests and because the effect of water on the rubber was, we believe, negligible during the short interval of test. When the tank was filled with water and finely cracked ice the temperature could be held readily between zero and 2° C., and when the electric heaters were in operation the water could be held very close to 100° C. The heat transfer to or from a small sample of rubber in water is very rapid. It was found that a stock produced the same stress-strain curves whether immersed

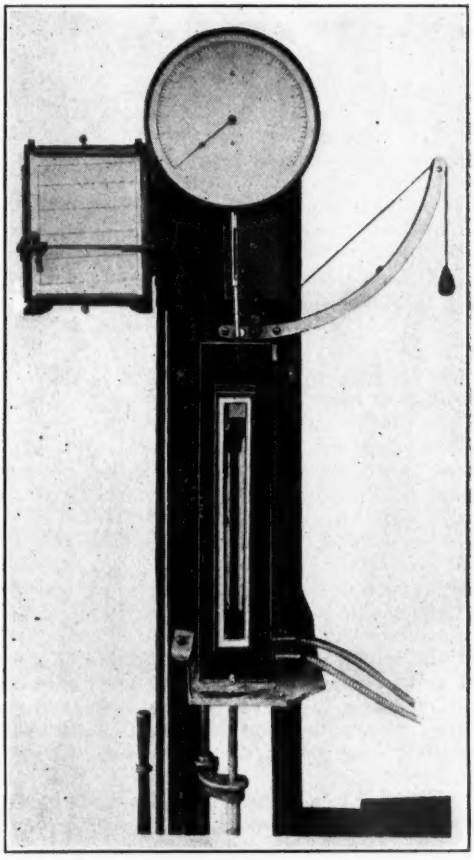


Fig. 2

only a few seconds or for 15 minutes before stretching. To secure fair uniformity the samples were immersed at no tension ten seconds in the hot or cold water before stretching. Five seconds immersion would have given practically identical results.

The jaws or grips for holding ring-shaped test pieces on the testing machine each consisted of 2 ball-bearing spools ½-inch in diameter spaced horizontally 1¼ inches between centers. This type of jaw was adopted after numerous tests with single spool jaws and with spools of different diameters. It was found that

these spools rolled freely under the conditions of heat and cold used throughout the test and there was no indication of cutting the sample at the point of contact with the spools.

In order that the operator could apply the rubber test rings to the jaws without dipping his hands into the hot or cold liquid, a slip joint was provided in the bar to which the top jaw was attached. This slip joint permitted both the top and bottom jaws to be raised above the level of the liquid in the tank when the pulling bar was brought to its topmost position. This loose coupling or additional movement of the upper jaw accounts for the autographs starting at a fixed point above the base line of the graph sheet.

Test Specimens

Dumb-bell test pieces could not be used because it is not possible to follow the marks showing elongation accurately on the test piece after it is submerged in the liquid and also because the autographic record of a dumb-bell piece does not represent the true stress-strain curve. It is most convenient to use a ring-shaped test piece, and in this work a ring 6 inches in mean circumference, 1/10 of an inch wide and approximately 1/10 of an inch thick, was used. Test pieces of this kind were made by cutting rings out of flat mold-cured sheets, using for the purpose cutting dies such as are now standard equipment on the market.

Stress-Strain Curves

The physical property of vulcanized rubber which is most affected by change in temperature is that property usually referred to as stiffness, but in reality what is being measured is the stress required to stretch the test piece a certain percentage of its original length, and the curve showing the relation between the stress and the percentage elongation is known as the stress-strain curve. The exact definition of longitudinal stress is the ratio of force to cross sectional area and in this work it has been calculated to pounds per square inch. Similarly longitudinal strain is defined as the ratio of the total elongation to the original length.

Accordingly the physical property that was measured and studied in these experiments was the stress-strain curves of various compounds maintained at different temperatures during the test. In using a ring shaped specimen and spool jaws of the type described it is possible to get an accurate autographic record of the stress-strain curve with one of the standard autographic recording devices which is a part of the Scott rubber testing machine. The thickness or gage of the test rings varies considerably, but it is possible as usual to determine that gage and to calculate the tensile per square inch at any elongation up to 500 per cent from the autographic curve. As the machine and chart are constructed the figures on the Y axis or abscissae represent per cent elongation of the test piece and the figures on the X axis or ordinate represent pounds pull as measured, indicated, and recorded by the testing machine. The graph sheet used on the testing machine is not laid out in exactly rectangular coordinates, but the lines in the direction of the X axis deviate by a slight angle from a horizontal base line. This chart is so laid out as to compensate for the slight downward movement of the upper jaw of the test machine while the sample is being stretched.

Figure 3 shows an original chart with stress-strain autographs drawn by the testing machine. It should be noted that the cross-

section lines of this original chart are not exactly rectangular, but are slightly off square as explained in the previous paragraph.

Figure 4 shows autographic stress-strain curves for samples tested at 0° and 100° C. These test pieces were cut from one sheet representing a typical tread stock containing rubber, zinc oxide, carbon black, sulphur, accelerator, antioxidant, and softener, given what was considered to be a proper cure. It may be noted when the sample is elongated to 400 per cent, the line AB represents the stress when the sample was stretched at 100° C. and

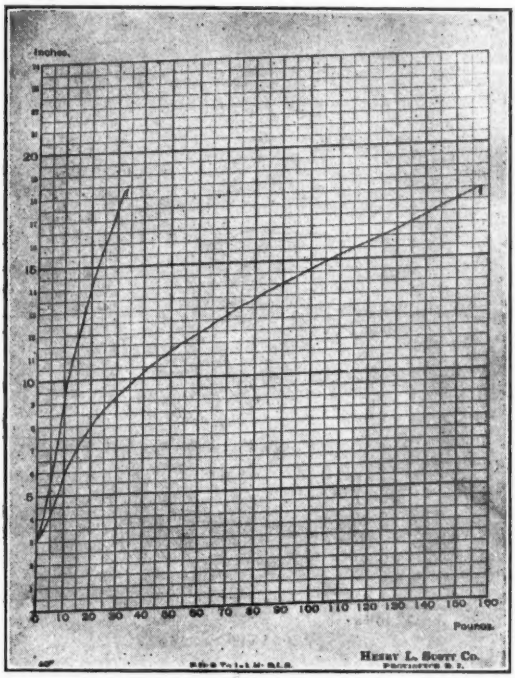


Fig. 3

the line AC represents the stress when the sample was stretched at 0° C. The bow or "belly" seen in the curves at a point from 0 to about 30 per cent elongation is real and is not due to the sluggishness of the testing machine. The bow or "belly" would be in the opposite direction if it were due to the sluggishness of the machine.

If a spiral steel spring replaces the rubber test piece and the stress-strain curve is drawn, the curve is very nearly a straight line from the origin with an indication of a slight sluggishness of the testing machine, which may be minimized by proper lubrication.

It may be determined from Figure 4 that the relative spread between the 0° and 100° C. stress-strain curves is not constant for all elongations. An attempt has been made to show the relative separation of the stress-strain curves in Figure 5. Stresses at different elongations have been plotted as taken from the 0° and

100° C. stress-strain curves and the ratio of the stress at 100° to the stress at 0° C. at each elongation has been shown as a percentage figure. The percentage figure has been drawn to the left indicating a decrease in stress in passing from 0° to 100° C. and it is seen from Figure 5 that the ratio of the stress at 100° to the stress of 0° C. is the greatest at the lower elongations. If no stress were required to stretch a piece of rubber at 100° C. then the line AB in Figure 4 would be zero and the ratio of AB

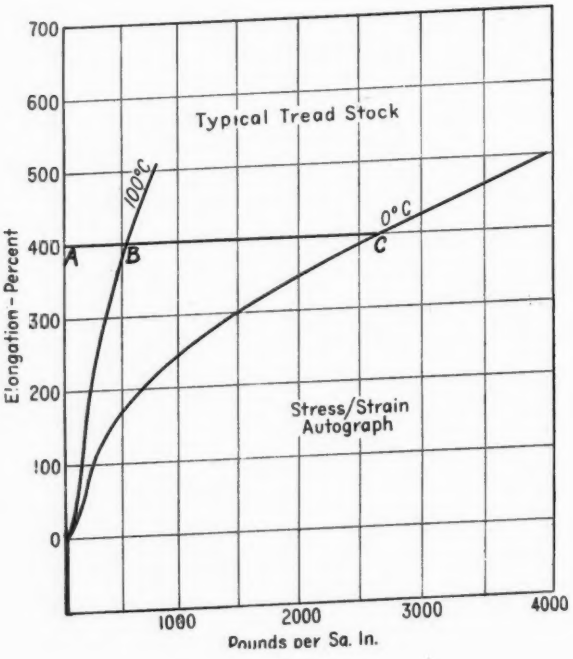


Fig. 4

to AC would be zero and the corresponding percentage line in Figure 5 would be zero. In other words, the shorter the percentage line in Figure 5 the greater is the relative separation of the 0° and 100° C. stress-strain curves.

It must be admitted that the possibility of a mechanical error in the machine at the lower elongation is greatest and it should also be stated that the exact rate of change and shape of curves differ for different compounds, and the samples shown are merely what we would term general illustrations taken from typical compounds in use today. Probably the error of the autographic stress-strain curves due to various factors is within the limit of plus or minus 5 per cent. For most of our further work we have made comparisons of stress at the 400 per cent elongation.

Various Rubbers

The effect of temperature on the stress-strain differs for various rubbers. In Figure 6 is shown the stress at the 400 per cent

elongation taken at both 0° and 100° C. in the case of nine different rubbers in one simple compound, together with the ratio of

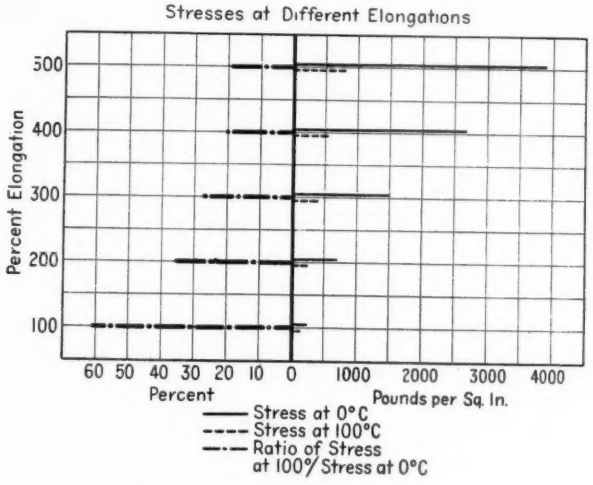


Fig. 5

the stress at 100° to the stress at 0° C., expressed as a percentage figure. Again it should be remembered that the shorter percentage lines indicate the greater relative spread between the stress-strain curves at 0° and 100° C. These nine rubbers were compared in three compounds. The first compound consisted of 100

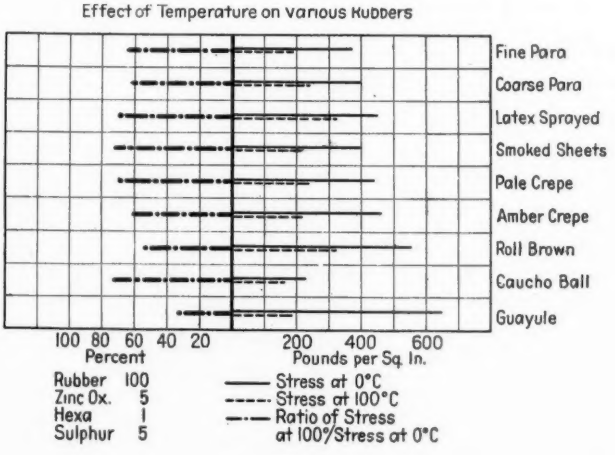


Fig. 6

rubber and 10 sulphur. The second compound 100 rubber, 8 sulphur and 3 aniline. The third compound 100 rubber, 5 zinc

oxide, 1 hexa and 5 sulphur. In the further work smoked sheet has been used in all compounds.

The variation in temperature effect on different rubbers may be shown in a more striking way in Figure 7 by showing the stress-strain curves on fine para and guayule tested at 0° and

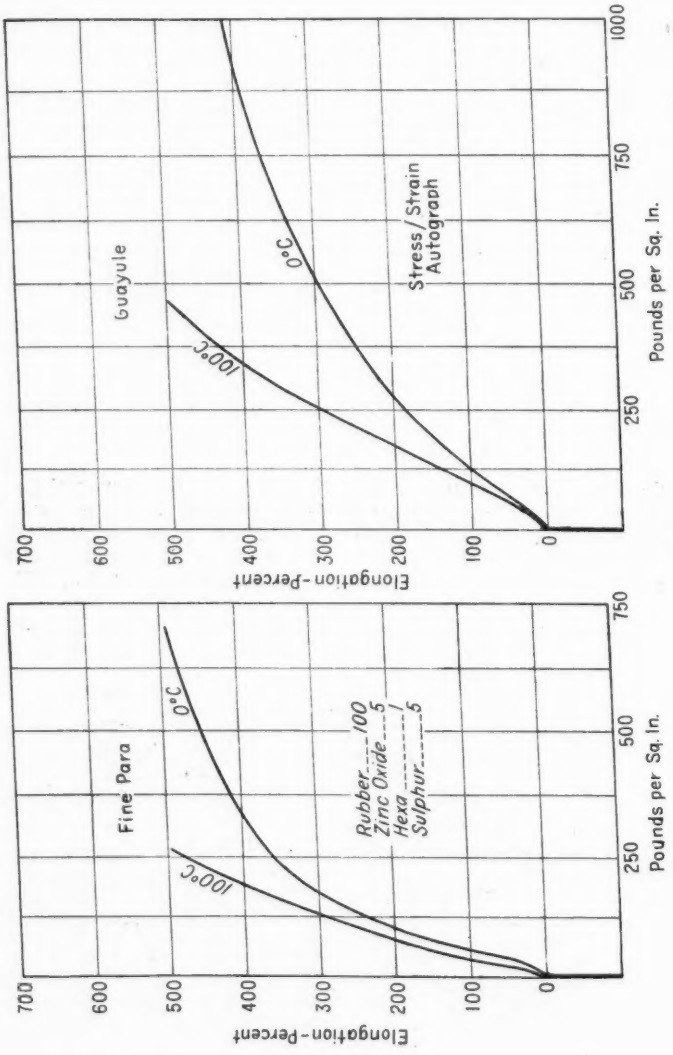


Fig. 7

100° C. Probably it would naturally be expected that inasmuch as the guayule contains a considerable percentage of resin, it might be more greatly affected by a change in temperature. This is true of guayule in both a cured and uncured state and is evidenced in the uncured state by its unusual softening qualities on a warm calender.

Various Temperatures

Tests have been made on stocks at various temperatures between 0° and 100° C. and in Figure 8 the autographic stress-strain curves are shown for a typical tire tread stock at 0°, 20°, 40°, 60°, 80° and 100° C. These curves are spread out in a fan shape arrangement just about as one would expect.

The stresses at the 400 per cent elongation at different temperatures have been read from Figure 8, and these data put in a

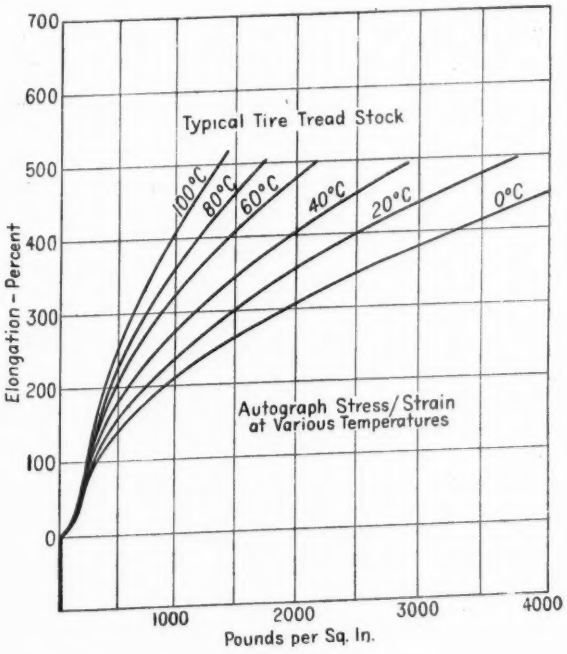


Fig. 8

different form in Figure 9, where the temperatures in degrees Centigrade from 0 to 100 are indicated on the Y axis and the horizontal lines or those parallel to the X axis indicate the stresses at the different temperatures, and from this Figure 9 it is readily seen that the rate of change of stress decreases as the temperature increases within the temperature limits used in this experiment.

Time of Cure

From the beginning of these experiments it was quite evident that the length of time of cure is an important factor in affecting the spread of these 0° and 100° C. stress-strain curves, so in all this work each stock has been given a range of six cures at one temperature and some stocks have been given a range of cures at two or three temperatures. Dumb-bell shaped test pieces have been used in making the usual tensile and elongation breaking tests in air and from these data what has been considered to be the best cure or cures have been selected and used in making

calculations and drawing conclusions from the stress-strain curves made at different temperatures.

If the tests on the dumb-bell pieces in air have shown that the stock had a fairly flat curing curve, and it is difficult to pick what one considers to be the best cure, two or even three cures have been taken in some cases and the average of these used in drawing final conclusions. The stress-strain curves at 0° and 100° C. have however been drawn on samples of stock of all six cures in every case, though what is obviously the undercures and overcures have not been used in making calculations pertaining to stress-strain data.

The method of selecting a proper cure can best be illustrated by Figure 10. Assuming that a stock has been given a range of

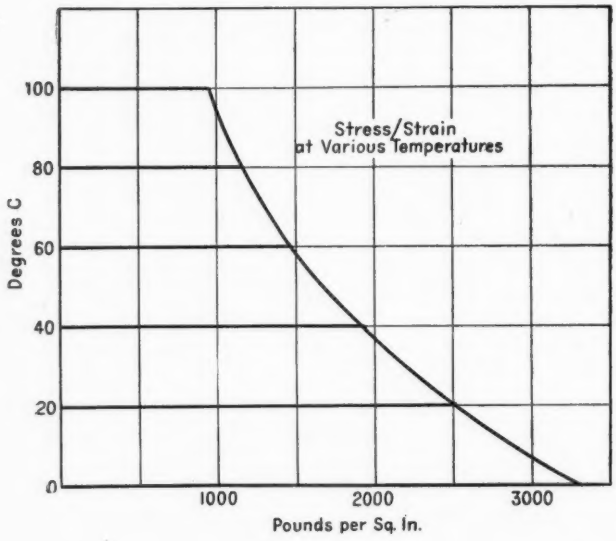


Fig. 9

six cures 15-30-45-60-75 and 90 minutes at some fixed temperature, the tensile strength of these cured stocks is determined by the usual method of breaking dumb-bell shaped pieces in air. The tensiles per square inch are then calculated and plotted in the form of a curve as shown in Figure 10.

A range of cures is always taken that will include both an undercure and an overcure. From the tensile curve for this range of cures the proper cure or the cure that we have selected for use in making our calculations of the stress-strain relations at 0° and 100° C. would be one such as the 45 minute cure in this case. If the tensile curve over the range of cures is a fairly flat line, and it is difficult to pick one proper cure, then three cures have been picked such as the 30-45 and 60 minute cures, and the average results obtained on the three cures used in calculating stress-strain relations of the tests which were made at 0° and 100° C.

A typical tread stock has been cured at 10-15-30-40-60 and 75 minutes in a laboratory slab or sheet mold at 141° C. The stress-

strain curves at 0° and 100° C. are then drawn autographically on samples of stock given each of these six cures. The stress at the 400 per cent elongation at both 0° and 100° C. is then read from these autographic curves. These stresses are shown in Figure 11. The ratio of the stress at 100° to the stress at 0° C. is then shown as a percentage figure drawn to the left representing a decrease in stress or stiffness of the stock as the temperature is raised from 0° to 100° C. It is to be noted from that figure, as it would be expected, that the stress at 400 per cent increases as the cure progresses when the stress is measured at either 0°

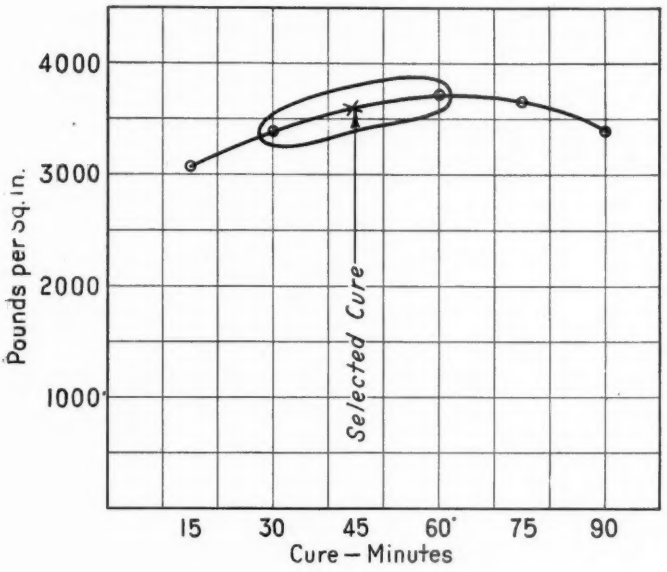


Fig. 10

or 100° C. It is also to be noted that the ratio of the stress at 100° to the stress at 0° C. increases as the cure progresses.

Sulphur Variation

It is an old story that there was originally much complaint before vulcanization with sulphur was known that raw rubber was quite stiff when cold and quite soft when hot. Vulcanization with sulphur went a long way toward eliminating that trouble. The effect of the amount of sulphur used is shown in Figure 12. Compounds were mixed with various amounts of sulphur from ½ to 6 per cent on the rubber, given a range of six or more cures and what was considered to be the best cure used in calculating the data shown in Figure 12. The stresses at the 400 per cent elongation at 0° and 100° C. are shown in Figure 12. The compounds containing the low amount of sulphur were naturally not well cured, but it is interesting to see that the amount of sulphur which gives the minimum spread between the 0° and 100° C. stress-strain lines is 2 or 3 per cent. If one goes to the extreme of using 40 or 50 per cent of sulphur, making hard rubber,

the ratio of the stress at 100° to the stress at 0° C. is undoubtedly very low. Likewise if one goes to the other extreme of using 0 per cent of sulphur the ratio of the stress at 100° to 0° C. is

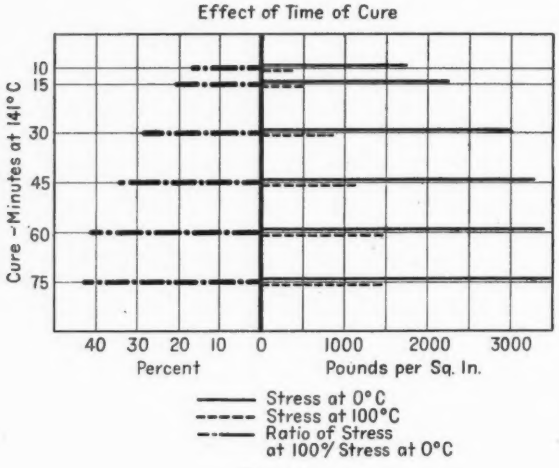


Fig. 11

fairly low. It seems confusing that the spread between the 0° and 100° C. stress-strain curves should decrease as the cure progresses and that the spread between the 0° and 100° C. stress-strain curves should increase as the amount of sulphur added to

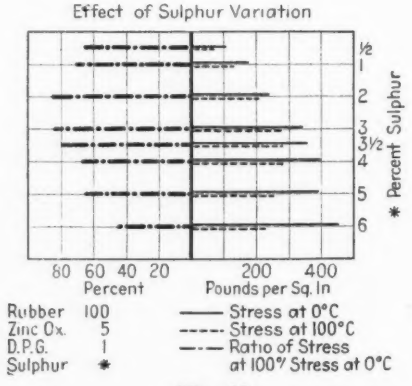


Fig. 12

the compound is increased. No determinations of combined sulphur have been made.

Accelerator Variation

Apparently if one obtains approximately the correct cure, the variation in the amount of accelerator used is not as important

as the variation in the amount of sulphur used in its effect upon the spread of the 0° and 100° C. stress-strain curves.

In Figure 13 data are shown where the sulphur is held constant at 4 per cent on the rubber excepting in the last compound where the sulphur is reduced to 2 per cent. The amount of accelerator is varied from ½ to 2 per cent. Again approximately the correct cures are used as well as can be determined. The stresses at the 400 per cent elongation at 0° and 100° C. are indicated and the ratio of the stress at 100° to the stress at 0° C. is again shown

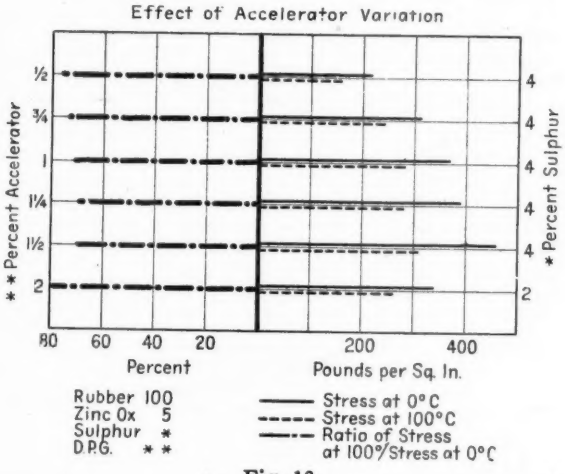


Fig. 13

as a percentage. It is interesting to note when the sulphur is reduced from 4 to 2 per cent with high acceleration that the spread between the 0° and 100° C. stress-strain curves is decreased.

Fatigue Tests

An attempt has been made to make what might be termed a fatigue test on a typical tread stock properly cured, these tests being made at 0° and 100° C. A ring specimen was put on the testing machine, stretched once to 500 per cent elongation and returned to its original position and this action repeated several times. Inasmuch as the ring-shaped specimen is 6 inches in mean circumference it is necessary to elongate the piece a total of 15 inches in order to obtain 500 per cent elongation. The stretching bar operates at the rate of 20 inches per minute and returns to its uppermost position at the same rate without any appreciable interval of time for reversal between the end of the stroke at either the upward or downward position of the stretching. It is readily seen from Figure 14 that after the sample has been stretched 3 times at the 0° C. the stress-strain curve begins to approach a constant and this final curve is much different from the curve obtained on the initial test or the first time the sample is stretched.

Set Test

The above test has been changed slightly as shown in Figure 15 in which case the sample is stretched to 500 per cent elongation

and held in that position 5 minutes, then brought back to the original position of no tension for 5 minutes; again stretched to 500 per cent elongation, held another 5 minutes and this repeated several times. The same thing is done at both 0° and 100° C., and

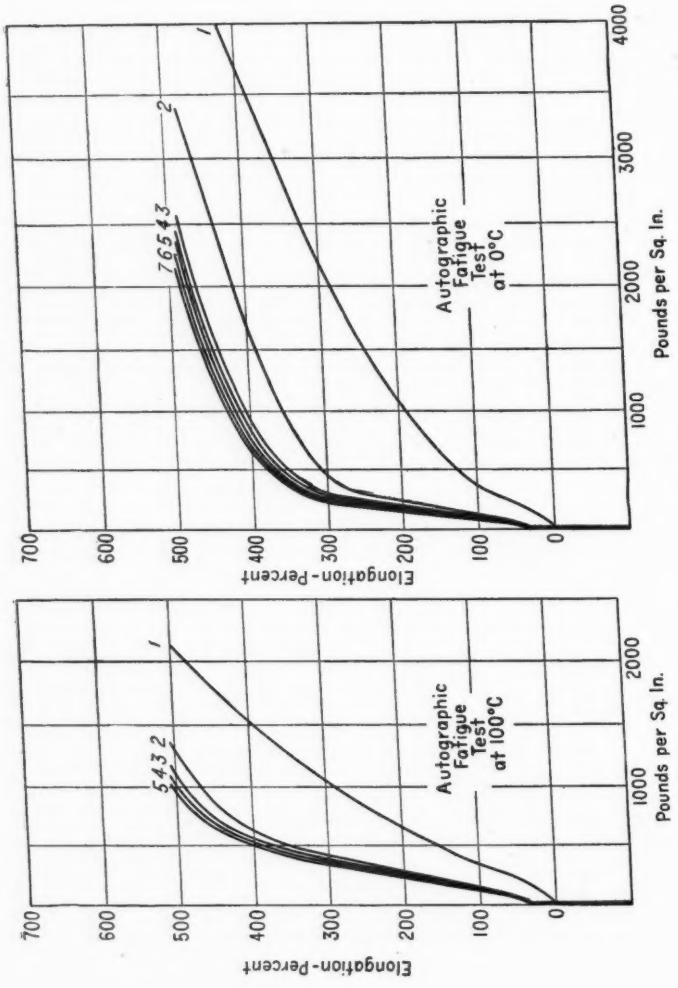

Autographic Fatigue Test at 0°C
Pounds per Sq. In.
Elongation - Percent
Autographic Fatigue Test at 100°C
Pounds per Sq. In.
Elongation - Percent

Fig. 14

it is noted that the stress-strain curves spread out a greater distance in this set test than they do in the so-called fatigue test.

Friction Test

Figure 16 shows the results on stripping tests made on belting at 0° and 100° C. in water and 25° C. in air. The jaws of the testing machine separated at the regular rubber testing rate of 20 inches per minute, which is too fast for friction testing, and this accounts for some of the irregularities in the curves. It is

to be noted that the friction pull at 100° C. is about half the pull at 0° C.

Overcures

The effect of an overcure is one of the most interesting things that has been met in this work. It has already been noted that the length of time of cure is an important factor in the spread of these 0° and 100° C. stress-strain curves. It is also notable that in an overcured compound the stress-strain curve drawn at 0° C. may not sharply indicate an overcure, but that the same overcured stock tested at 100° C. breaks exceedingly short.

In Figure 17 are shown the 0° and 100° C. stress-strain curvs for a compound that has been cured at 60 and 90 minutes at 141° C. The 60 minute cure is possibly a very good one and there is nothing in either the 0° or 100° C. stress-strain curve to indicate anything wrong. But when that same stock is cured 90 minutes at 141° C. and tested at 100° C. it breaks at an elongation of slightly over 200 per cent, while the same stock tested at 0° C. shows a fairly normal stress-strain curve with no indication of shortness. This breaking short at 100° C. is not an experimental error, accident or freak, but it occurs in any overcured stock. Some stocks have a much wider curing range than others, but it appears that testing at 100° C. shows up an overcure definitely different from any other method now generally known. It would seem that the effect of overcure might be very serious on the service qualities of a stock subjected to temperatures as high as 100° C.

Antioxidants

An attempt has been made to show in Figure 18 the effect of an antioxidant as used in a typical tread stock. The stocks were made identically the same except that one contained an antioxidant. Both stocks were cured at 15-30-45 and 60 minutes at 141° C. All four cures of both stocks were aged 7 days in a Geer oven at 70° C. The 15 minute cure could undoubtedly be called an undercure and the 60 minute cure an overcure. After 7 days aging in the Geer oven stress-strain curves were drawn on all these stocks at 0° and 100° C. The upper half of the figure shows a successive shortening of the stress-strain curves as the cure progressed from 15 to 60 minutes. This shortening occurs in the case of both the 0° and 100° C. curves, indicating that the Geer oven is not primarily overcuring the stock, for if such were the case only the 100° C. stock would break short, while the 0° C. stock would still have a good elongation, but instead it indicates that the Geer oven is causing aging or deterioration, that is, not overcuring in itself. It also shows that the longer cures deteriorate faster than the shorter cures in a Geer oven.

The lower half of Figure 18 shows that the addition of an antioxidant helps preserve physical properties of the stock, particularly when given an overcure, preventing it from breaking short. It might also be added that the addition of an antioxidant does not in any way affect the relative spread between the 0° and the 100° C. stress-strain curves.

Future Work

Data have been obtained in the form of autographic stress-strain curves at 0° and 100° C. on about 250 compounds, including 4 secondary vulcanizing agents, 12 antioxidants, 20 softeners, 30

accelerators, 36 fillers and some other special materials. These data will be subject matter for future publication.

Apparently most of the laboratory work that has been done on this general subject to date has been analytical or diagnostic in nature. The second phase of the work normally would be to de-

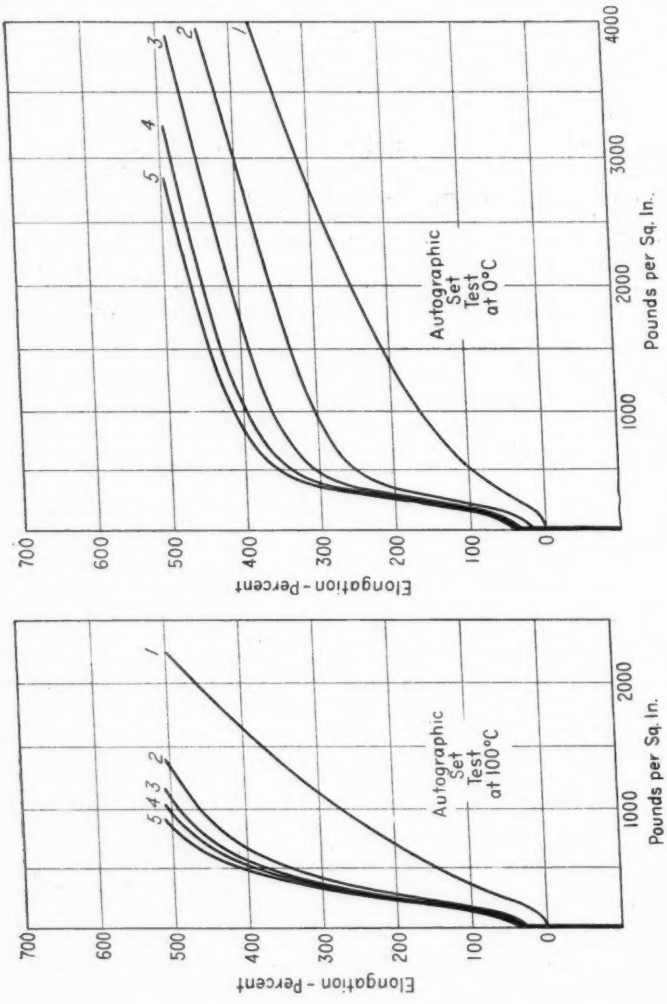


Fig. 15

termine a remedy for the condition if we consider that it is a troublesome matter that the stress-strain properies of vulcanized rubbers change with temperature. For some purposes it might be a splendid improvement in compounding if a rubber stock could be made that would give constant stress-strain properties at all temperatures within reasonable ranges. Some work has been done in that direction, and it is undoubtedly possible to make compounds which when properly cured will actually show higher stress-strain

figures at some elongations when tested at 100° C. than when tested at 0° C. Further work along that line is now in progress.

It is now planned to construct a new testing machine equipped with a tank 48 inches in length that will permit the stretching of a test piece to the breaking point, and to equip this tank not only with electric heaters for heating the liquid, but also with re-

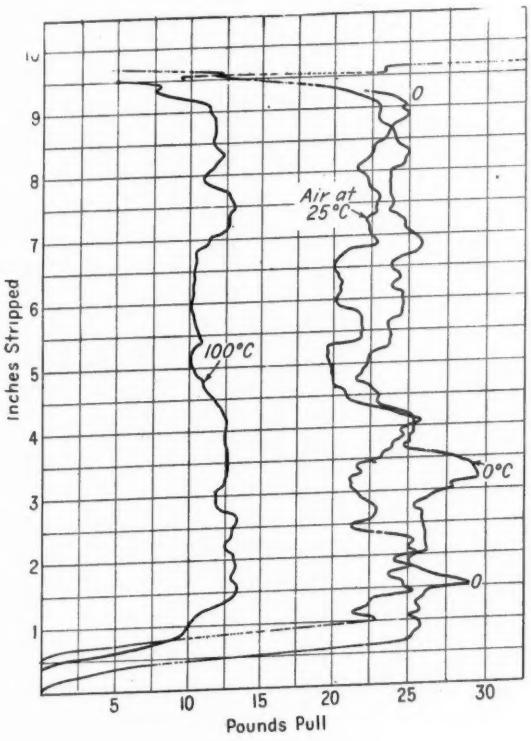


Fig. 16

frigerating coils for cooling the liquid, and to use liquids for heating and cooling the rubber test piece to a wider range of temperatures than the 0° and 100° C. used in these experiments.

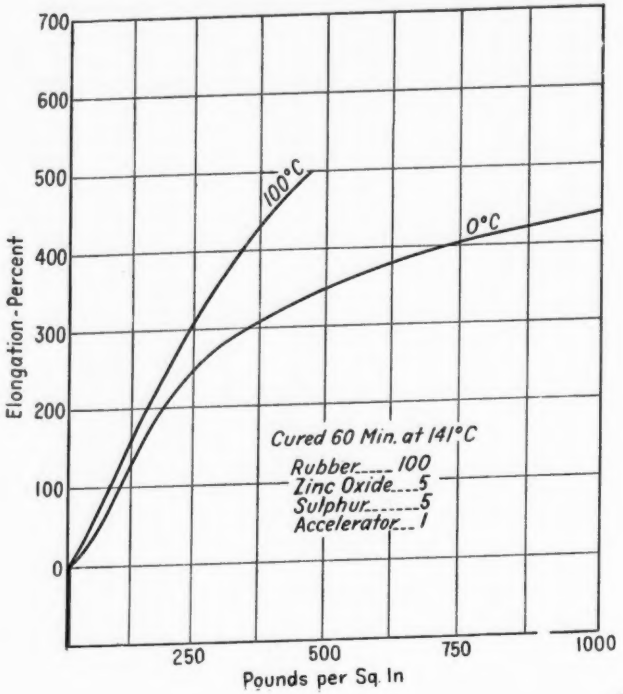
Summary

A method has been devised for testing rubber at various temperatures by putting a simple attachment onto a commercial testing machine.

Wide variations have been found in the stress-strain curves on the same stock at different temperatures.

The stress-strain properties at different temperatures vary for different rubbers.

The state of cure causes a wide variation in tests at various temperatures.



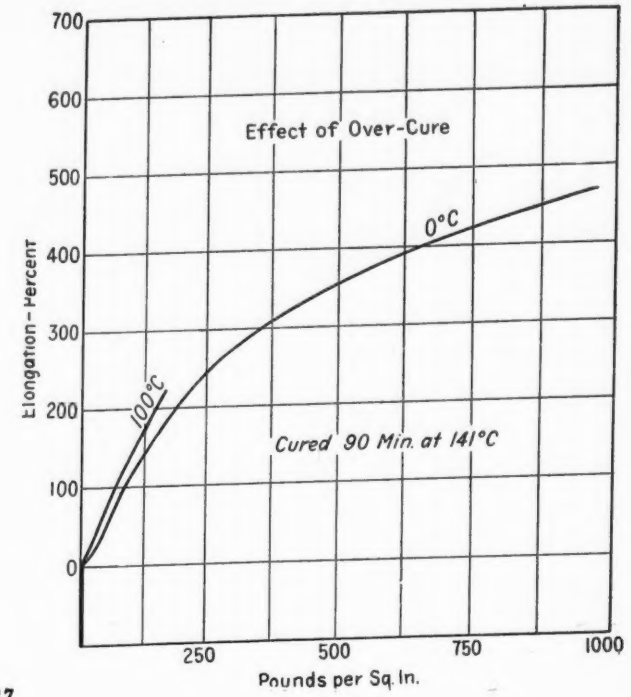


Fig. 17

TWO TREAD STOCKS EACH GIVEN FOUR CURES

TWO TREAD STOCKS EACH GIVEN FOUR CURES
AND ALL CURES AGED 7 DAYS IN GEER OVEN

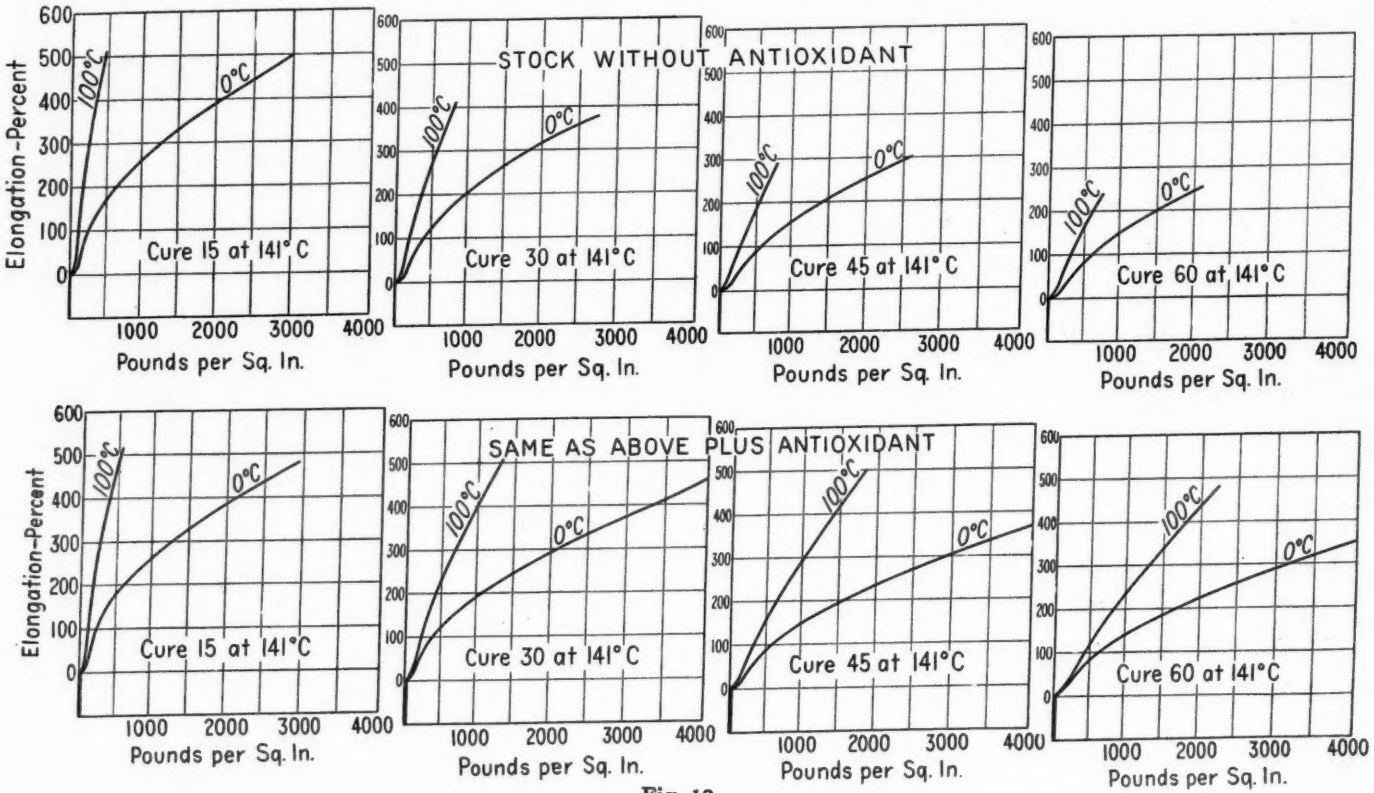


Fig. 18

The amount of sulphur used is a factor in the stress-strain relationship at different temperatures.

Successive stresses on the same piece of rubber show large decreases after the first or second stress.

Stripping tests on frictions show much lower strength at 100° C. than at 0° C.

Overcures are indicated prominently when stocks are tested at 100° C.

Artificially aged rubber tested under these conditions shows a very marked deterioration which may be offset by anti-oxidants.

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Reënforcement of Rubber by Fillers[1]

John T. Blake

SIMPLEX WIRE AND CABLE CO., BOSTON, MASS.

A new theory of pigment reënforcement is presented, in which a reënforcing filler is defined as one which forms a bond with the rubber matrix that is stronger than the matrix itself. A molecular tensile curve substantiates the conception. The mechanism of filler dispersion is considered, and the work of Langmuir and Harkins is applied to rubber. Calculations of the quantity of dispersing agents and of the heats of wetting conform to experimental values. The means of extending the reënforcement of rubber by carbon black is discussed.

VULCANIZED rubber as ordinarily used in commercial articles has fillers or pigments compounded in it. The fillers fall into two general classes—those which improve the quality of the product and those which dilute the rubber and only lower the cost per unit volume. The members of the first class are called reënforcing fillers and are chiefly carbon black, zinc oxide, magnesium carbonate, and certain clays. The members of the other class are called diluents and can be almost any material desired. Whiting, lithopone, and baryte ares examples of this type of filler.

A good accelerated pure-gum stock will give a tensile strength of 3000 pounds per square inch. When 30 volume per cent of carbon black is added, the compound develops a tensile strength of 4000 or more pounds per square inch. Coincident with the increase in tensile strength, there is a de-

[1] Presented before the Boston Group, Rubber Division, American Chemical Society, May 9, 1928.

crease in stretch and an increase in resistance to abrasion, stiffness, and resilient energy.

Theory of Reënforcement—Previous Work

Wiegand has studied the reënforcement of rubber by carbon black and has proposed several methods of evaluating the effect. He concluded from a theoretical viewpoint that the proof resilience—that is, the amount of mechanical work necessary to stress 1 cubic inch of rubber to rupture—is the best index of improvement.[2] This increase in proof resilience is conveniently measured by determining the area beneath the stress-strain curve and converting to suitable units. The improvement in quality is usually measured by an increase in resistance to abrasion.

He next proposed the concavity factor as another index of improvement. This is defined as the ratio of one-half the tensile product to the proof resilience. This value becomes unity when the tensile curve is a straight line.

These two methods give values for the effect of a filler at a single concentration. To express the effect of the filler over the useful range of loading, the "A" function is used.[3] This "A" function is the relation between proof resilience and volume loading.

If the "A" function is plotted for a reënforcing filler, it rises from the value of the base mix to a maximum and then decreases. The volume loading at which it crosses the ordinate of the base mix is the concentration of the filler at which reënforcement ceases. The "Δ A" function is the integrated excess of the "A" function over that of the base mix, and is a measure of the reënforcing value of a filler.

Wiegand, however, has chiefly been concerned with the evaluation and use of the reënforcing effect in a practical way rather than with the mechanism of it. A consideration of the mechanism is essential if we are to extend the range of its effect. Reënforcement may be expressed as an increase in tensile strength. Spear has offered a theory of carbon black reënforcement that is the only real attempt to date to explain this phenomenon. He postulates that when rubber is stretched the resulting lateral contraction develops very thin films of rubber matrix surrounding the harder rubber aggregates. These films ultimately become quite thin and are more solid and rigid. When gas black is dispersed in rubber, its fine state of division develops these thin rigid films markedly, with the result that the rubber is stiffened and strengthened.

Wiegand[4] has suggested that lithopone whose particle size approximates that of a reënforcing filler should, from this theory, exhibit much the same reënforcement. This, of course, is contrary to experience.

[2] *Can. Chem. J.*, **4**, 160 (1920).
[3] Wiegand, IND. ENG. CHEM., **17**, 939 (1925).
[4] *Trans. Inst. Rubber Ind.*, **1**, 152 (1925).

Piling Concept

It has been suggested that in the average rubber compound there is only a small fraction of the possible amount of filler that could be incorporated and still have each particle insulated from the others by a film of rubber.

If we consider the filler particles to be uniform spheres arranged in cubical piling and the particles separated from each other by an infinitesimally small film of rubber, they will occupy $\overline{\wedge}/6$ of the total volume. In other words, it should be possible to incorporate 109.91 volumes of filler into 100 of rubber before this state is reached.

If the particles of filler are arranged in tetrahedral or pyramidal piling, the fraction occupied by them becomes $\overline{\wedge}/3\sqrt{2}$. In this manner, 285.56 volumes of filler could be incorporated before the individual particles came in contact.

There is a third type of piling which might be called triangular piling—a form of pyramidal piling. In this system, the fraction occupied by the filler is equal to $\overline{\wedge}/2\sqrt{6}$, and 178.76 volumes of filler can be compounded into 100 volumes of rubber with perfect dispersion.

There is a fourth system of piling which is probably an intermediate phase of the transition from cubical to tetrahedral or triangular piling. It might properly be called rhomboidal piling, the centers of the particles forming a right rhombus. The fraction occupied by the filler would be $\overline{\wedge}/3\sqrt{3}$, and 152.91 volumes of filler would be associated with 100 volumes of rubber in a perfect dispersion. This system is probably unstable and would revert to the tetrahedral system easily.

Free and Bound Rubber

According to the piling concept, there should be a certain amount of rubber "bound" by or associated with the filler particles, depending on the volume fraction of the filler and the form of piling. When a perfect dispersion is obtained with the volumes of filler as calculated above, the whole of the rubber is "bound." For a given system of piling, the ratio between the bound rubber and the amount of filler is determined by the figures calculated above and is constant for any filler concentration. When the bound rubber is 100 per cent, the compound should be rigid, hard, have a strength approaching that of mild steel, and be incapable of extension without rupture. It is the ultimate in compounding.

It may be safely postulated that the fillers are in themselves inextensible. The elasticity and attendant phenomena of a rubber compound are therefore vested in the rubber matrix. When a compound is prepared so that the maximum amount of filler is incorporated according to a piling system and all the rubber is bound, there is no mechanism by which the compound can stretch without rupture. In order to obtain an elastic rubber, there must be present less than this maximum

amount of filler and thus give less bound rubber. The free (or unbound) rubber is available for stretching and the above statement may be amplified by saying that the ability to stretch, or the elasticity of a compound, is vested in the free rubber of the matrix.

Mechanism of Rupture of Rubber

When a test piece of rubber is stressed, it stretches and ultimately breaks. The break in the material can occur in one of three places—in the filler particle, at the joint between the particle and the matrix, or in the matrix itself. Of course, if the break were in the particle, there would be an accompanying break in the adjacent matrix and, similarly, if the break were in the joint, there would of necessity be a break in the adjacent matrix.

It is reasonable to suppose that when a rubber compound breaks there is no rupture of the average filler particle. If the filler particle were the weakest link, the addition of a filler

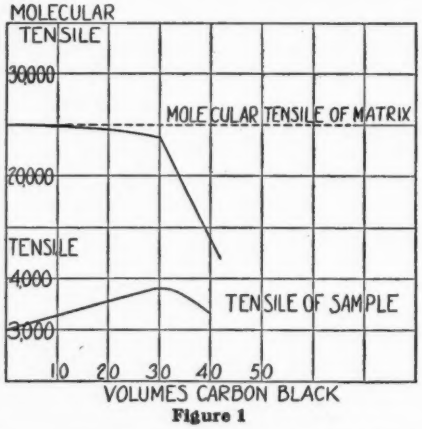

Figure 1

would weaken a compound in direct proportion to the amount added. When whiting is used as a filler, there is no question that it acts almost entirely as a diluent. It is one of the most inert pigments as Wiegand has shown.[3] Even in this case Endres[5] has shown microscopically that the break occurs between the filler particle and the rubber. Separation has been shown to start quite a while before rupture.

According to these ideas, fillers may then be divided into two classes—(1) those that form a bond with the rubber that is stronger than the matrix, and (2) those whose bond is weaker than the matrix. The first may be called reënforcing pigments and the second diluents. A compound with a reënforcing filler ruptures in the matrix alone, the line of break following the film of matrix between particles. The tensile strength calculated on the cross section at break is a measure

[5] Ind. Eng. Chem., **16**, 1149 (1924).

of the tensile of the matrix. It might be called the "molecular" tensile strength. The surface of the matrix along the line of break, of course, must be projected into a plane at right angles to the direction of pull to give the correct cross section. This becomes equal to the cross section as calculated from the stretch. The matrix, under the same conditions of cure and assuming no absorption of accelerator, etc., by the filler, should have the same molecular tensile strength at all conditions of compounding.

Reënforcement of Fillers

The tensile strength thus calculated should be a constant for any amount of filler as long as the reënforcing conditions are maintained. It should be independent of stretch. If we add greater and greater amounts of filler, we may come to a point at which the strength of the joint falls below that of the matrix. This may be due to two causes—(*a*) agglomeration of the particles of filler, or (*b*) failure of the rubber to form a bond with the particle. At this point the molecular tensile strength drops rather sharply.

If these tensiles be calculated from Wiegand's data[4] for carbon black, the phenomenon is well illustrated as follows:

Volumes Carbon Black	Stretch	Stretch + 1	Tensile	Product (Molecular Tensile)
0	7.60	8.60	3000	25,800
10	6.50	7.50	3250	24,400
15	6.25	7.25	3400	24,600
20	5.80	6.80	3400	23,100
25	5.45	6.45	3400	21,900
30	5.30	6.30	3800	24,000
35	4.20	5.20	3500	18,200
40	3.35	4.35	3300	14,400

The apparent reënforcing effect has not ceased at 40 volumes as the ordinary tensile is still 3300 pounds per square inch. If the values be plotted, the result is striking. (Figure 1) The molecular tensile is constant within probably the experimental error until the point where the bonding starts to fall below the strength of the matrix, when it starts to drop rapidly. In this particular case the reënforcement by this system actually ceases at 30 volumes pigmentation.

It may thus be seen that a so-called reënforcing filler does not reënforce in that molecular tensile of the matrix is not increased. It simply does not act as a diluent. The apparent reënforcing effect of the filler is due to its shortening effect. The tensile as calculated on the original cross section does increase and the shortening effect balances this increase in calculating the molecular tensile. The shortening effect is caused by the amount of free rubber being decreased by the increase in the amount of filler. The amount of free rubber is a straight line function of the added filler, so the stretch should be a straight line function of the amount of filler over the reënforcing range. Such a theoretical line should go through the origin as the stretch is zero when the free rubber is zero. When reënforcement ceases, the break occurs in the filler rub-

ber joint and the stretch is thereby shortened beyond the calculated amount. This is illustrated for the above data in Figure 2.

Theoretically, with an inert filler the tensile strength and stretch disappear when the free rubber becomes zero.

Wiegand gives part of a proof resilience curve for both whiting and barytes, which should follow very closely the same course. The irregularities of the particles of commercial fillers would lower the value in practice below the various values as calculated from the different forms of piling. The small rise in the curves at the beginning of pigmentation shows that there is a slight reënforcement that ceases almost immediately.

Particle Size

There are numerous references in the literature to the effect that particle size is the controlling factor in the reënforcing value of a pigment. It is claimed that the smaller the average size of the particles the greater the total surface energy per

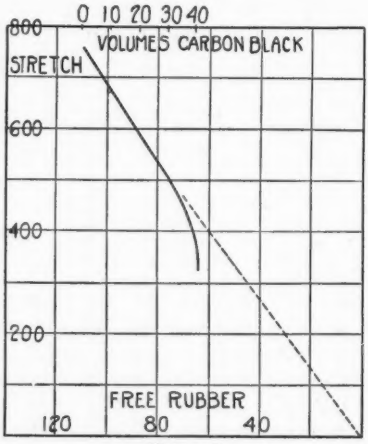

Figure 2

unit volume of filler. Reënforcement is presumed to be proportional or related in some manner to this total surface energy. From the foregoing point of view, it becomes evident that it is the intensity of surface energy in the filler-rubber bond or the energy per unit area of bonding that is the controlling factor in reënforcement. Particle size should have nothing to do, directly, with the reënforcing power of the pigment. This explains why lithopone and other substances of small particle size are practically useless as reënforcing fillers. Particle size may indirectly have an effect if the character of the surface changes with particle size. The reënforcement value of a pigment depends only on the specific material, the character of its surface, and the completeness of dispersion obtained. There are only two kinds of joints of interest—those stronger and those weaker than the matrix.

Mechanism of Filler Dispersion

Failure of complete dispersion of a filler to be obtained and maintained at all concentrations in rubber is due to two factors—(1) agglomeration or flocculation of the filler particles, and (2) failure to obtain complete wetting of the filler by the rubber and strong adhesion of the particle to the matrix.

It is well known that certain dissolved substances tend to concentrate at a surface. The addition of 1 per cent sodium oleate to water lowers the surface tension to about one-third its original value. There is probably little change in the composition of the interior of the liquid, but the concentration of the dissolved material at the surface of the liquid has had a profound effect on it as evidenced by the decrease in surface tension. Bancroft has called attention to the fact that shaking a rennet solution destroys its ability to coagulate milk. The enzyme has been concentrated in the surface of the bubbles in the froth. An aqueous solution of amyl alcohol contains a lower concentration of alcohol than the froth from the same solution.

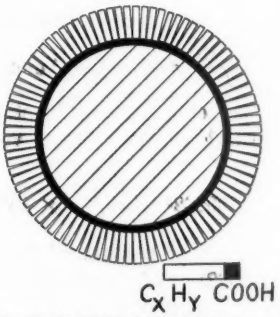

Figure 3—Carbon Black Particle

To form stable emulsions or suspensions, a protective colloid is usually employed. In such a case the dispersing agent concentrates from the solution to the surface of the peptized material. The question arises as to whether there is a protective colloid in rubber which controls and determines the completeness of the dispersion of carbon black and other reënforcing fillers in rubber.

The proteins and albuminoids of rubber are not soluble in the rubber hydrocarbon and would be incapable of migrating to and concentrating at the surface of filler particles. The inorganic salts and unsaponifiable portion of the resin are very probably without action as protective colloids.

The saponifiable portion of rubber resin consists chiefly of fatty acids or their esters. If they were the dispersing agent, each perfectly dispersed carbon black particle would be surrounded by a monomolecular layer of fatty acid adsorbed on the surface. From the work of Langmuir and Harkins on the orientation of molecules in surface layers, such a film would

have the molecules of acid directionally adsorbed. The hydrocarbon portion would extend into the rubber and the acid portion would be on the surface of the particle. The particle would appear as in Figure 3.

From previous considerations, the reënforcement of carbon black ceases in the neighborhood of 30 volumes in 100 volumes of rubber. The amount of fatty acid required to disperse completely that amount of carbon black in rubber according to the above theory may be calculated.

From Langmuir's[6] work on monomolecular films of fatty acid on water, we may obtain figures for the average cross section of an oriented molecule. In such a case the carboxyl group extends into the water and the hydrocarbon residue is in the air. The stearic acid molecule has an average cross section of 22 square Ångström units. Palmitic acid has a cross section of 21 square units. This value would be quite constant for any monobasic straight chain fatty acid, since a change in the number of carbon atoms alters only the length of the hydrocarbon chain. The cross section of the molecule would not be changed.

If stearic acid is used in the calculations, in 1 sq. cm. of an oriented monomolecular film there would be

$$\frac{10^8 \times 10^8}{22} = 4.6 \times 10^{14} \text{ molecules}$$

The average diameter of a carbon black particle is probably 0.2μ or 0.00002 cm.[5,7] The average volume of a particle would be

$$\frac{\overline{\lambda}}{6} \times 0.00002^3 = \frac{4 \times \overline{\lambda}}{3} \times 10^{-15} \text{ cc.}$$

The average surface of a carbon black particle would be

$$\overline{\lambda} \times 0.00002^2 = \overline{\lambda} \times 4 \times 10^{-10} \text{ sq. cm.}$$

If we use the ratio as discussed above, 1 cc. of rubber would have compounded in it 0.3 cc. carbon black. 0.3 cc. carbon black would contain

$$\frac{0.3 \times 3}{4 \times \overline{\lambda} \times 10^{-15}} = \frac{0.9 \times 10^{15}}{4} \text{ particles}$$

The surface area of this number of particles would be

$$\frac{0.9 \times 10^{15} \times 4 \times 10^{-10}}{4\,\overline{\lambda}} = 0.9 \times 10^5 \text{ sq. cm.}$$

The number of molecules of stearic acid necessary to form an oriented monomolecular film on the surface of this 0.3 cc. carbon black would be

$$4.6 \times 10^{14} \times 0.9 \times 10^5 = 4.15 \times 10^{19}$$

The molecular weight of stearic acid is 284. In 284 grams of stearic acid there would be 6.06×10^{23} molecules. The weight of acid necessary to form this layer would be

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[6] *J. Am. Chem. Soc.*, **39**, 1848 (1917).

[7] Spear, Colloid Symposium Monograph, 1923, p. 332; Norris, *India Rubber World*, **77**, 55 (1927).

$$\frac{284 \times 4.15 \times 10^{19}}{6.06 \times 10^{23}} = 195 \times 10^{-4} = 0.0195 \text{ gram}$$

Plantation sheet contains about 3.0 per cent resins, of which about 80 per cent is saponifiable. The density of rubber is about 0.93, so that in 1 cc. of plantation sheet there would be 0.022 gram of fatty acid available.

The two values agree within about 10 per cent which is quite gratifying, considering the type of calculation involved. Of course, in practice, even within the range considered, dispersion is not absolutely complete, and the figure given is a limiting value. In addition, a certain amount of stearic acid reacts with the zinc oxide to give soluble zinc to activate the accelerator.

This principle alters somewhat the theoretical figures obtained for the various systems of piling. The layer between particles was considered to be infinitesimal. The minimum layer of material that can be placed between adjacent filler particles and still obtain a perfect dispersion would consist of two layers of oriented stearic acid molecules and a layer of rubber molecules.

The stearic acid molecule is about 23×10^{-8} cm. long. The dimensions of the unit cell of rubber have been determined by various observers through the agency of x-rays. The value varies some, but the average thickness is about 7×10^{-8} cm.[8] The previous figures when recalculated on this basis, using particles 0.2 μ in diameter, are:

System of Piling	Old Basis	New Basis
Cubical	109.91	93.84
Rhomboidal	152.91	126.74
Triangular	178.76	145.62
Tetrahedral	285.56	217.03

When carbon black is dispersed in rubber according to this theory, the change in heat content should be equal to the heat of wetting of the carbon by the fatty acids and not the heat of wetting by the rubber. The heat of wetting is the heat absorbed when a solid surface and a liquid surface are brought together. It is the same quantity as the integral heat of adsorption of a vapor at its saturation pressure. The amount of heat has been shown to be proportional to the surface. Gaudechon[9] has measured the heat of wetting of sugar char (which is nearly pure carbon) by acetic acid. The heat of wetting is 6.0 gram-calories per gram of carbon. Hock's[10] figure for the heat of adhesion of carbon black (Micronex) at 30 volumes per 100 volumes rubber concentration is about 5.1 calories per gram of carbon. The values are not only of the sample order of magnitude, but the agreement is quite close.

[8] Katz, *Kolloid-Z.*, **37**, 19 (1925); Ott, *Naturwissenschaften*, **15**, 320 (1926).

[9] *Compt. rend.*, **157**, 209 (1913).

[10] *India Rubber J.*, **74**, 454 (1927).

Applications

As a general proposition, a long chain polar compound with the required solubilities would be a good dispersing agent. Long chain alcohols would be about as effective as the fatty acids, since they both have a large hydrocarbon portion and an end hydroxyl group.

The above considerations give an explanation for a number of empirically discovered facts.

Stearic acid is frequently added to high carbon black stocks and it has been tacitly assumed that the dispersion is improved. Reclaimed rubber contains a comparatively high acetone extract. These resins would act as dispersing agents, and this would explain the fact that reclaimed rubber may be economically used in high grade rubber products.

Wiegand in his British patents on high carbon black compounds uses pine tar dissolved in a solvent such as toluene as a dispersing agent. The solvent serves to introduce the tar quickly into the rubber and then it evaporates. Pine tar contains a considerable amount of fatty acids and high molecular weight alcohols.

Bierer's experiments[11] with zinc oxide and carbon black pastes may be put on a good theoretical basis. He formed a stiff paste of the pigment and a solvent such as kerosene. The addition of a very small amount of various substances completely liquefies the paste. The rubber resins or stearic acid used to cause liquefaction form a monomolecular oriented film on the particle surfaces and disperse the pigment. Wool grease would have the same sort of action, since it consists chiefly of fatty acids and cholesterol, which is a long chain alcohol. He states that "there is a minimum proportion of thinning agent to pigment below which 'liquefaction' will not take place. This varies with each combination (thinning agent and pigment)." This minimum is the quantity needed to form a monomolecular film and would be a definite ratio for a given filler and reagent.

Methods of Research

The method of improving the rubber, on these principles, consists in delaying the break in the molecular tensile curve by increasing the range over which dispersion is complete. This may be accomplished by changing the rubber so that there is complete adhesion between the filler and the rubber and that the filler does not agglomerate. This bonding is apparently a function of the dispersing agents naturally occurring in the rubber and those added deliberately. The effectiveness of high amounts of various long chain polar compounds on the dispersion of high volumes of carbon black and other fillers should be ascertained. The use of a matrix that will disperse clay well offers a valuable field. The removal of adsorbed gases on fillers might render a desirable improvement in dispersions.

[11] *Trans. Inst. Rubber Ind.*, **3**, 174 (1927).

Conclusions

Wiegand's "Δ A" function, as represented by the double integral of tensile with respect to elongation and volume of a pigment over the base mix, is a practical means of expressing the reënforcing effect of the filler. On the other hand, the volume range over which the bonding of the filler is greater than the strength of the rubber matrix gives a better understanding of the condition of the filler in the rubber.

Apparently, the importance of fatty acids and other polar compounds in dispersions can be put on a sound theoretical basis.

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Heat Transfer in the Vulcanization of Rubber[1]

T. K. Sherwood[2]

HOOD RUBBER COMPANY, WATERTOWN, MASS.

Temperature lag in the heating of rubber articles is found to cause marked non-uniformity of cure in the product. The theory of "unsteady state" heat flow is discussed, and a method described for analyzing data on temperatures in rubber being heated. From data on the temperatures at different times during the heating process and on the relation between the rate of cure and the temperature, it is shown how the resulting curing effect at different points in a solid rubber object may be calculated. A new water cure process for tires is described which is very effective in reducing the non-uniformity of cure caused by the temperature lag effect, and at the same time appreciably reduces the necessary curing time.

THE vulcanization of rubber goods involves heating the rubber compound to definite vulcanization temperatures, and frequently the problem of obtaining the best cure is primarily a problem in heat transfer. The type of heat transfer involved is the so-called "unsteady state" flow, as contrasted with heat transfer in boilers, condensers, and other equipment where the temperatures at all points in the apparatus remain relatively constant. As heat flows into the rubber a temperature gradient is set up from surface to interior, the points farthest from the source of heat

[1] Paper presented before the Boston Group, Rubber Division, American Chemical Society, May 9, 1928.

[2] In collaboration with T. M. Knowland, development manager, Hood Rubber Company.

being at the lowest temperature. Moreover, since the rubber through which the heat flows is being continually heated, the flow of heat passing planes parallel to the surface decreases as it flows towards the interior, and the temperature gradient is not linear. The interior is at first heated much more slowly than points near the surface. The modern tendency is towards short cures with highly accelerated stocks, but in many cases the shortening of the curing time is limited by the slowness with which the heat penetrates the rubber, making it impossible to cure the interior of the rubber mass in a short time, even though the compound be highly accelerated.

Temperature Lag Effect

The temperature lag effect is found in the heating and cooling of all solid substances. It gives trouble in quenching steel billets, causing the surface to be hardened to a greater

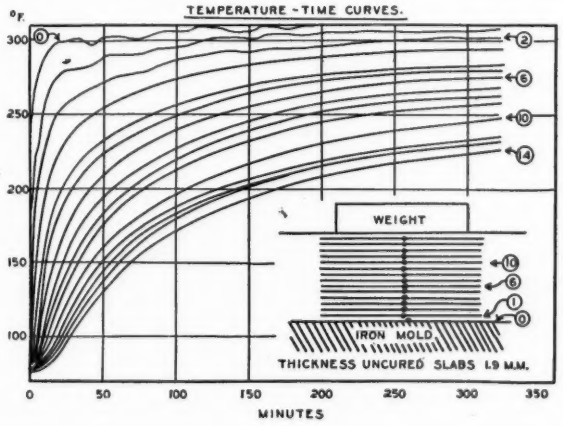

Figure 1

degree than the interior. The effect is greatest in large objects or in materials of low thermal conductivity. Temperature lag is important in heating all but the thinnest rubber goods, since the thermal conductivities of rubber compounds are relatively low, and is especially noticeable in heating heavy rubber articles such as truck tires. Figure 1 illustrates the magnitude of the effect for various thicknesses of red tube stock. Thermocouples were placed between successive layers of uncured stock, each 0.075 inch (1.9 mm.) thick and about 12 × 15 inches (30 × 38 cm.), and the pile laid on a hot mold and weighted down. The mold face was maintained nearly constant electrically and the temperatures at the different thermocouple positions were recorded at short intervals of time. As may be seen from this figure, point 4 which was 0.3 inch (7.6 mm.) from the mold face required 1 hour to reach 239° F. (115° C.), the melting point

of sulfur, while points an inch (25.4 mm.) from the mold had not reached this temperature after 5 hours. It is not surprising, therefore, that cross sections of thick rubber objects show wide variations in cure.

The temperature lag in the laboratory vulcanization of a rubber sample is very different from that of plant vulcanization of a heavy rubber product, using the same compound. As an example, assume that laboratory tests indicate that for a particular accelerated compound the optimum cure at 40 pounds steam pressure (141° C.) is 15 minutes; it is quite possible that the point at which this compound is used in a thick rubber article may never reach the melting point of sulfur in the first 15 minutes of heating. The question then arises—how long should a compound subjected to a large temperature lag effect be heated to obtain the optimum cure?

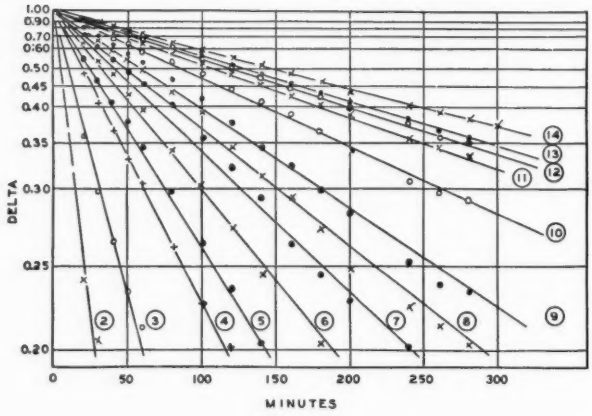

Figure 2

In order to answer this question for a given case, we must have two things: (1) experimental data or accurate calculations giving the temperature-time curves for the points in question; and (2) a means of predicting the length of this rising temperature cure that will give results comparable with those obtained in the laboratory tests at a practically constant temperature.

Unsteady State Heat Flow

The theory of unsteady state heat flow is dealt with more or less fully in many books on advanced mathematics. The work involved in using the results was so great, however, that they were seldom put to practical use until 1923, when Gurney and Lurie[3] showed that they might be greatly simplified by the use of plots of the important variables. These authors used the variables Δ and τ, which are defined as follows:

[3] IND. ENG. CHEM., **15**, 1176 (1923).

$$\Delta = \frac{\text{unaccomplished temperature change at any time}}{\text{total possible temperature change}}$$

$$\tau = \frac{Kt}{x^2}$$

K is the thermal diffusivity of the solid (thermal conductivity divided by the product of density and specific heat); t is the time of heating from the start; and x is a linear dimension such as thickness in the case of a sheet. Gurney and Lurie[3] give plots of Δ *vs.* τ for points in different positions in several solid shapes, and for different values of the surface

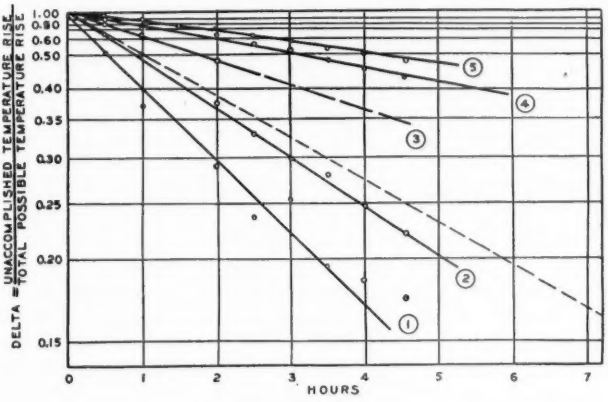

Figure 3

resistance to heat flow. This surface resistance to heat flow is negligible when heating rubber in molds.

In order to compare the theoretical function with actual data, Figure 2 was made with the ordinate scale so changed as to force the theoretical curve of Δ *vs.* τ for a "semi-

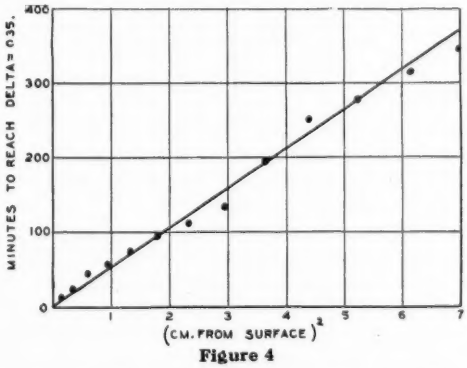

Figure 4

infinite solid" to be a straight line. The line shown dotted on Figure 3 is the theoretical line for which the abscissa scale represents values of τ. Thus data plotted on this figure as Δ *vs.* τ should fall on this dotted line; or, from the definition of τ, it is seen that data plotted as Δ *vs.* time should fall on

straight lines the slopes of which depend on the distance from the mold face x, and the value of K. That this is the case is shown by the data plotted, which were obtained exactly as those shown in Figure 1, but are for 0.25-inch (6.35-mm.) slabs of vulcanized tread stock, initially at 89° F. (32° C.), being heated by a mold at 268° F. (131° C.). By comparison of the lines representing the data with the theoretical (dotted) curve (for which the abscissa scale represents values of τ) the values of the thermal diffusivity, K, may be determined. Figure 3 shows the data of Figure 1 on tube stock plotted as Δ *vs.* time, using the special ordinate scale, and it is seen that approximate straight lines result. Since the slopes should be inversely proportional to the square of the distance from the mold face, then by similar triangles the time required to reach any given value of Δ should be proportional to the square of the distance from the mold face. Figure 4 shows the time to reach a value of Δ of 0.35, as read from Figure 3 plotted against the square of the thickness x, and it is seen that a linear relation is approximated. The failure of the points to fall on a smooth curve is doubtless due to the displacement of the thermocouples in the soft uncured rubber being heated, which error is magnified on this plot as the thickness x is squared. The best line through the points, however, shows that that point 1 inch (2.54 cm.) from the mold face reached a Δ of 0.35 after 340 minutes; from the theoretical curve a Δ of 0.35 corresponds to a τ of 2.44; hence

$$\frac{K \times 340 \times 60}{(2.54)^2} = 2.44$$

from which the thermal diffusivity, K, is 0.00077 in c. g. s. units. This value is for red tube stock; from several sets of data similar to those plotted in Figure 2 an average value of 0.00075 was obtained for vulcanized tread stock. These values compare well with that of 0.00069 given by Williams[4] for cured rubber.

Calculation of Curing Effect

The general theory outlined above makes it possible to predict temperature curves for solid shapes for which the theoretical relations of Δ and τ have been worked out, but is of no direct value for the case of such a complicated solid shape as a tire having an intricate tread design. For such a case it is best to obtain experimental data on the temperatures at various points in the tire being heated. From one set of such data it is possible to predict accurately the time-temperature curves for the same tire being cured at various temperatures, and to estimate fairly accurately the curves for other tire sizes.

An idea of the magnitude of the temperature lag effect in tires may be gained from Figure 5, which shows data on temperatures in a 29 × 4.40 balloon being cured on an air

[4] Ind. Eng. Chem., 15, 154 (1923).

bag in a watch-case vulcanizer. Similar data on temperatures in tires being vulcanized have been obtained by Cranor[5] and by Perks and Griffith.[6] Although the tire tested was of light construction and the steam used was at slightly over 300° F. (149° C.), the point next the air bag required 25

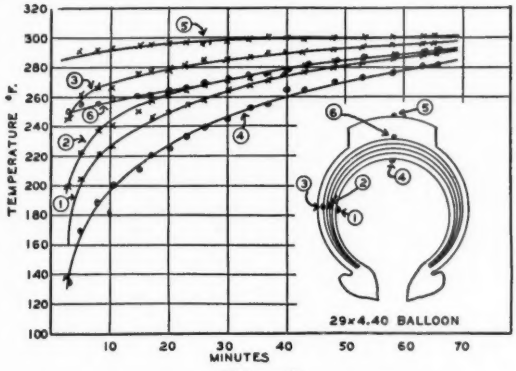

Figure 5

minutes to reach the melting point of sulfur. Large tires show correspondingly greater temperature lag effects, Cranor's data on an 8 inch cord tire showing that over 2 hours were required for some points to reach the melting point of sulfur. The effect is extreme in solid tires where the rubber thicknesses are much greater.

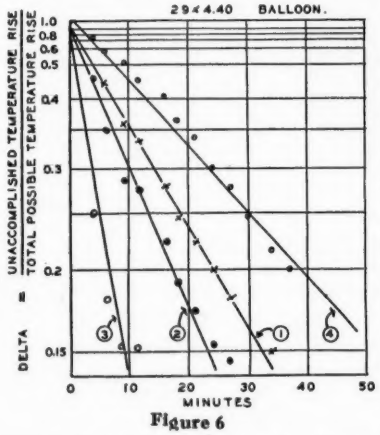

Figure 6

Data on temperatures in tires may be analyzed in a manner similar to that described above for the experimental mold. The data of Figure 5 are shown replotted in Figure 6 as Δ *vs.* time, again using the special ordinate scale which causes the theoretical curve to be a straight line. Approximate straight lines result which are seen to fall in order of the distances of the thermocouples from the mold face. By comparison with the location of the thermocouples used to get these data, straight lines could be drawn on Figure 6 to represent other points in the same tire, or even in other tire sizes. Then, by working backward from the values of Δ read from this plot, it would be possible to predict the temperature-time curves for any mold temperature.

[5] *India Rubber World*, **68**, 709 (1923).
[6] *India Rubber J.*, **67**, 25 (1924).

The important effects of the temperature lag in vulcanizing tires are two: (1) The curing time is extended to that necessary to vulcanize the rubber at the points farthest from the mold; (2) unevenness of cure in the product must result unless built up of an impractical number of compounds having different rates of cure. In most cases a properly cured tread surface can only be obtained along with an undercured friction stock, and if the carcass is properly cured the tread will be overcured. Perhaps the most striking illustration of the unevenness of cure is the appearance of tire cross sections which have stood long enough to bloom; many of them show the section near the tread surface to be black and tough, whereas the lower portion of the tread near the breaker shows excessive blooming. This effect is common in all sizes of tires cured on air bags, and is illustrated in Figure 7. The unevenness of cure may be decreased by the "step up rise" of steam temperature, but in so doing the time of cure is lengthened.

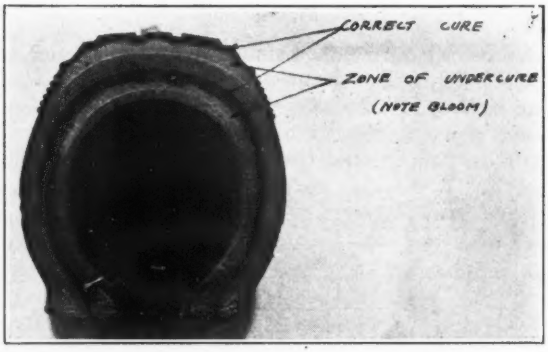

Figure 7—Cross Section of Tire Showing Unevenness of Cure

Comparison of Laboratory and Factory Data

As suggested above, it is not only desirable to have data or accurate calculations of the temperature-time curves for points in the rubber article being vulcanized, but it is necessary to be able to compare laboratory test data with the results of the rising temperature cure in the factory. According to Whitby,[7] the rate of vulcanization increases approximately 2.3-fold for each 10° C. or 18° F. rise in temperature. Data on a red tube stock and a tread stock indicate the factors to be 2.8 and 2.5, respectively. Using an average value of 2.5 for this factor—i. e., assuming the rate of vulcanization to increase 2.5-fold per 10° C. or 18° F.—Figure 8 has been constructed, showing the rate of vulcanization relative to that at 286.7° F. (142° C.) as a function of temperature. This plot gives the minutes at 286.7° F. equivalent to 1 min-

[7] "Plantation Rubber and the Testing of Rubber," p. 321.

ute at any other temperature. By means of this plot the rate of cure at any point in the rubber object may be plotted against time, provided the temperature-time curve for the point in question is known. Such a plot of cure *vs.* time has been made as shown in Figure 9, the several curves representing points at different distances from the mold face, for the case of heating the tube stock slabs for which the temperature data are given in Figure 1. The resulting curing effect for any point, being the integral of the rate of cure times the time of heating, is represented by the areas under the curves in Figure 9. Figure 10 shows these areas[8] or, in other words, the resulting curing effect, plotted against the distance from the mold face, for three different times of heating. This plot illustrates in a striking manner the difference in resulting

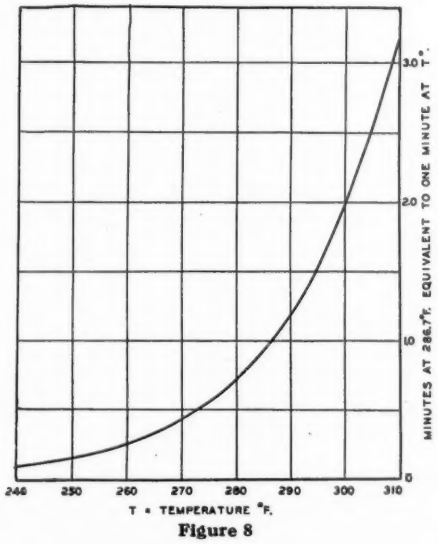

Figure 8

cure at various distances from the mold face in a thick rubber slab. In most vulcanized articles the surface is overcured and the interior undercured. The tensile product will therefore be at a maximum at some intermediate point, as indicated by Figure 11. Moreover, this maximum value of the tensile product will be the maximum tensile product for the particular compound used. This plot has been drawn by using the cure distribution curve of Figure 10 for 100 minutes' heating time, and referring to a typical tensile product–time curve, the cure distribution being replotted as tensile product in relative units *vs.* distance from the mold face. The position of the maximum shown will depend on the time of

[8] Sheppard and Wiegand, IND. ENG. CHEM., **20**, 953 (1928), used this same method of evaluating a variable temperature cure, as did also Perks and Griffith, *loc. cit.*, in England several years ago.

heating, retreating into the interior as the time of heating is increased.

Except at one point, the rubber is either overcured or undercured, and the temperature lag effect therefore causes a

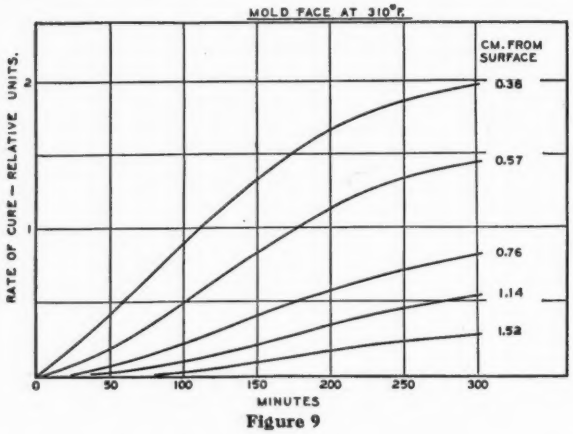

Figure 9

definite economic loss. The maximum tensile products for several typical tube stocks are shown plotted in Figure 12 against the compound cost in dollars per cubic meter, and it may be concluded that over the range in question the maxi-

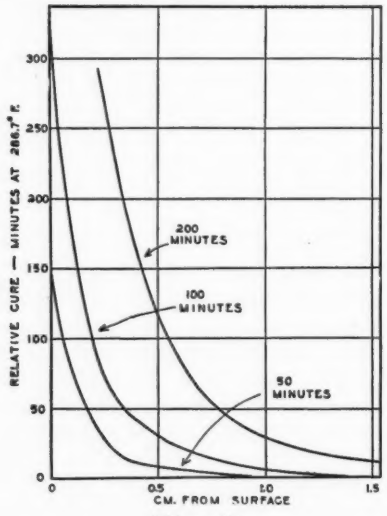

Figure 10

mum tensile product attainable is directly proportional to the compound cost. The tensile product curve of Figure 11, therefore, represents the relative value of the product at different distances from the mold face after 100 minutes' heat-

ing. The actual cost of the compound, however, corresponds to the maximum tensile product shown. What we pay for is represented by the dotted line, and the value of the product we get is represented by the lower curve. The area between the curves graphically represents the loss in dollars and cents involved, and the area under the lower curve, divided by the area under the dotted line, might be termed the "economic efficiency," which for the half-inch slab shown is about 35 per cent. The actual loss due to the temperature lag in vulcanization processes varies from zero in a very thin sheet to 60–70 per cent of the cost of the compound itself in thick slabs, and in tire treads the loss doubtless runs into millions of dollars annually. Furthermore, the surface must be overcured to get the necessary average tensile strength, making the product more susceptible to aging.

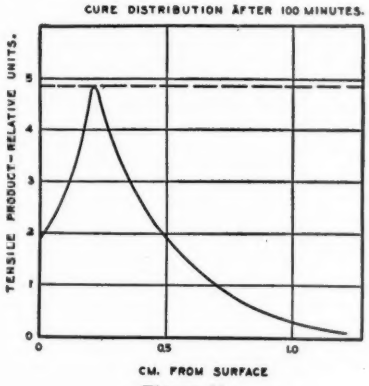

Figure 11

The serious mistake is frequently made of thinking that the optimum time for the vulcanization of a rubber article of appreciable thickness is identical with the optimum time of vulcanization of the laboratory test piece. As pointed out above, in extreme cases the interior of the object may never reach the melting point of sulfur in the same time which will give the optimum cure in the laboratory mold. Another common error resulting from neglect of the temperature-lag effect is in the calculation of the change in curing time necessary with a change in curing temperature. Figure 13 shows the resulting curing effects in relative units plotted *vs.* time, for the case of the rubber at the surface and for a point 0.3 inch (7.6 mm.) from the surface, for several different mold temperatures. The relative cure was calculated in a manner similar to that for the relative cures shown in Figure 10. The rate of increase of time necessary to effect a given cure at the surface and at a point 0.3 inch (7.6 mm.) from the surface is seen to be very different. If the surface is considered, a reduction in temperature of 18° F. (10° C.), say from 310° to 292° F.

(154° to 144° C.), would require the time of heating to be multiplied 2.5-fold, say from 140 minutes to 350 minutes; whereas if the point of 0.3 inch (7.6 mm.) from the surface is considered, the same decrease in mold temperature would require that the time of heating be increased from 140 minutes to only 183 minutes. Nomographic charts and plots have been prepared to simplify such calculations, but most of them neglect the effect of the rubber thickness, and are simply based on a two- to threefold increase in curing time for every 10° C. or 18° F. decrease in temperature. The use of such charts for thick objects, therefore, causes the necessary curing times when the temperature is increased to be underestimated, and similarly the curing times necessary when the mold temperature is reduced are often very much overestimated.

Water Cure Process

One obvious means of making the vulcanization effect more uniform is to build the thick rubber object in several layers, those farthest from the source of heat being most highly

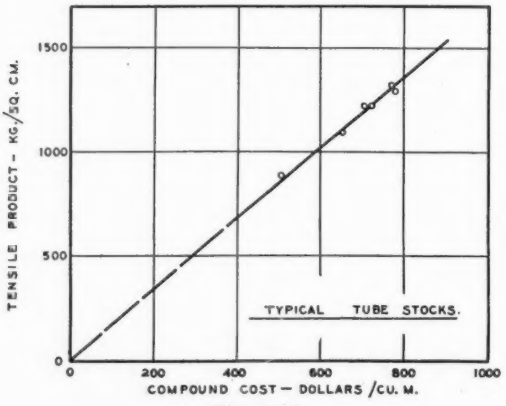

Figure 12

accelerated. However, the degree of acceleration necessary in the interior of the rubber slab is usually only guessed at, and is frequently underestimated. Another method of attack in the vulcanization of tires is the application of heat to the interior as well as to the exterior of the tire carcass. A recent development is a hot water curing method circulating water continuously through the air bag at a high temperature and pressure. The water is heated to over 300° F. (149° C.) and pumped into the air bag at one side, leaving at a point diametrically opposite, having passed through both semicircles in parallel. Since the supply of hot water is continuous, the air bag is not cooled down in the process of heating the tire carcass, as was the case with most of the water-cure processes.

A comparison of the temperature lag effect with air and

with hot water in the air bag is shown in Figure 14. The temperature-time curves are shown for a 29 × 4.40 balloon and on the same plot dotted curves indicate the average results of several tests for the same tire in the same mold with air in the bag. The temperatures of the rubber next to the mold face are practically the same for both methods of curing,

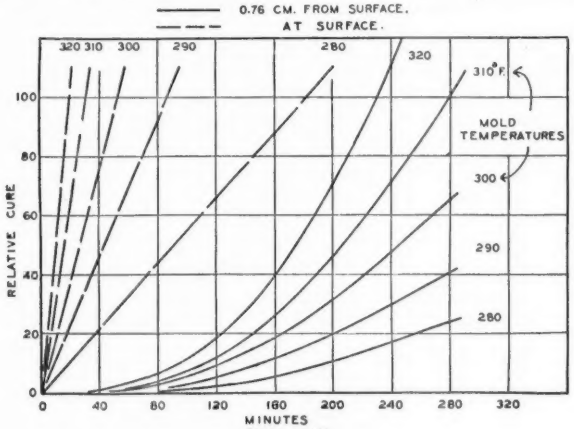

Figure 13

all temperatures in the tire being cured with air in the bag lie between curve 3 and dotted curve 4, whereas the extreme variations when hot water is used are from curve 3 to curve 5 or 2. The effect in increasing the uniformity of cure is obvious, and the time of cure may be expected to be greatly decreased. The percentage reduction in time of cure possible

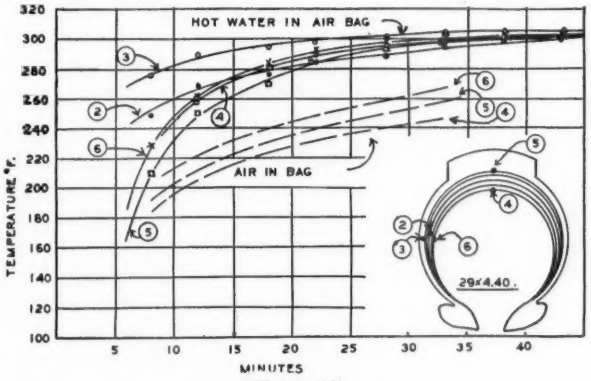

Figure 14

with this method will depend on the tire size and the time of cure necessary on the air bag; for the small tire tested the time of cure was reduced by almost 50 per cent. Furthermore, the uneven blooming effect of the tire cross sections is eliminated by the water-cure process, at least in the smaller tire sizes.

Acknowledgment

Acknowledgment is due H. A. Hands, who obtained the experimental data discussed, and to the Hood Rubber Company for permission to publish the results of these investigations.

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Determination of Sulfur in Rubber by the Perchloric Acid Method[1]

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In a search for a rapid and accurate method for determining sulfur in rubber it was found that oxidation of the sample by means of sodium peroxide in the Parr bomb is unsatisfactory when the sulfur content of the rubber is low because the samples that can be used for this purpose are too small for accurate results, or, if larger samples are used, the oxidation is incomplete.

The use of a mixture of nitric and perchloric acids, as described by Kahane, is also unsatisfactory; but with certain modifications the method may be made to yield very good results, and if fusions are unnecessary, it will save time and labor.

The chief modifications recommended are the use of a more dilute solution of nitric acid (equal volumes of the concentrated acid and water), allowing the rubber to dissolve completely on the steam bath before heating more strongly, then heating to gentle boiling until oxidation is complete, and finally destroying the residual nitric acid by means of hydrochloric acid.

The use of a larger flask (500 to 800 cc.) is also recommended, and suggestions are also made for the adaptation of this method to the analysis of those rubber compounds which contain barium, lead, etc.

It is recognized that this method, in its present form,

[1] Received April 16, 1928. Publication approved by the Director of the National Bureau of Standards.

has its limitations, and that there will undoubtedly be cases in which it will not be applicable. Nevertheless, in a large number of cases it should prove useful.

IN THE course of another investigation it was necessary to make a considerable number of determinations of the sulfur content of rubber. The amounts of sulfur were frequently small (less than 1 per cent) and a high degree of accuracy was desired as well as economy of time and labor. In all the methods now used the sulfur is converted in one way or another into sulfuric acid or sulfates and precipitated as barium sulfate. The chief problems are to destroy the organic matter completely and with the minimum expenditure of time and labor, and to convert the sulfur into soluble sulfate or sulfuric acid without loss of material. The two methods most generally adopted—namely, that of Waters and Tuttle,[2] and that of Kratz, Flower, and Coolidge[3]—are long and tedious. The first method particularly requires much attention. Moreover, it involves the addition of powdered sodium carbonate to concentrated nitric acid in a relatively small crucible; this operation produces a fine spray above the liquid, through which large volumes of gas must escape, making some loss inevitable. A method was therefore sought which would combine the advantages of speed and accuracy with the minimum of attention, and yet require no special skill and, if possible, no special apparatus in its application.

Except as otherwise stated, vulcanized rubber was used in the present work, and usually contained both free and combined sulfur. However, since all organic matter is completely oxidized in this method of analysis, it is not clear how vulcanization could make any difference in the results.

Objections to Parr Method

Oxidation with sodium peroxide in the Parr bomb would at first seem to answer these requirements almost ideally, since it not only destroys the organic matter in a very short time and under conditions which prevent loss of material, but also has the advantage common to all fusion methods of converting the sulfur into soluble form even in the presence of barium and lead compounds. This method is very satisfactory in the analysis of many organic compounds, but in the case of rubber a number of difficulties arise. In the first place, rubber is not so easily oxidized as some other organic materials, and for this reason it is difficult to start the reaction unless the composition of the charge is modified to facilitate the ignition of the mixture. In a pamphlet provided by the manufacturers of the Parr bomb it is suggested that this difficulty may be overcome by using only 0.1-gram sample of rubber adding 0.4 gram of sugar to the charge to

[2] Bur. Standards, *Circ.* **232**, 25; J. IND. ENG. CHEM., **3**, 734 (1911); Bur. Standards, *Bull.* **8**, 445 (1911).

[3] *India Rubber World*, **61**, 356 (1920); Bur. Standards, *Circ.* **232**, 26.

facilitate ignition. This quantity of sample is too small for an accurate determination of the sulfur in the ordinary gravimetric way, unless the proportion of the sulfur is high, and it is not feasible to increase materially the size of the entire charge on account of the limited capacity of the bomb. On the other hand, if the size of the sample is increased to 0.5 gram and no sugar is added to the charge, the oxidation of the rubber is frequently incomplete. Furthermore, the mixing of the charge is a tedious and often vexatious piece of work for the rubber tends to come to the surface of the charge during shaking or stirring. The oxidizing mixture and the disintegrated rubber therefore have to be sprinkled into the bomb in alternate layers. This operation is also difficult on account of the tendency of the rubber particles to become electrically charged and therefore to adhere to the sides of the bomb above the oxidizing mixture.

In general, the Parr sodium peroxide method was found to be unsatisfactory for sulfur determinations in rubber.

Advantages of Perchloric Acid Method

Kahane[4] has recently described a procedure for the rapid oxidation of the rubber sample which makes use of a mixture of nitric and perchloric acids and which, the author claims, prepares the sample for the precipitation of the barium sulfate in about 7 or 8 minutes. Although this method, in common with all acid-solution methods, is not applicable for general use in the presence of barium and lead compounds, the simple technic and the remarkably short time required for the operation would seem to make it worth while to examine its usefulness, at least in those cases where interfering elements are known to be absent.

After all, is it not possible that the advantages of the alkali fusion methods have been exaggerated? For instance, in many cases it is known that barium and lead compounds are absent. In other cases it is known that only barium is present in the form of its sulfate, which could readily be filtered off from the solution after the rubber has been dissolved, without interfering with the determination of the rubber sulfur in the solution in the usual way. If the barium is present in the form of the carbonate, all of the sulfur would probably be precipitated immediately, but in many such cases it could be determined with sufficient accuracy for most purposes by merely filtering off the precipitate, washing, and weighing as barium sulfate.

Note—In such cases a sulfur determination should also be run on the filtrate in the usual way, to cover those possibilities in which the amount of barium carbonate present in the rubber compound might not be sufficient to precipitate all of the sulfur. The precipitates might later be combined.

Rubber compounds which are known to contain only lead might be handled in a similar way, with due regard for the solubility of lead sulfate. Finally, in those comparatively

[4] *Caoutchouc & gutta-percha*, **24**, 13549 (1927); *C. A.*, **21**, 2817 (1927).

few cases in which a fusion is necessary, this can be done upon the precipitate which is filtered off from the acid solution obtained by oxidizing the rubber compound with the mixture of nitric and perchloric acids. In fact, this procedure might even have some advantages over the method of Waters and Tuttle, for it would avoid the possibility of loss involved in the addition of sodium carbonate to strong nitric acid, and it would certainly require less attention and care in the fusion operation.

Testing Accuracy of Method

Before adopting Kahane's procedure, however, it was considered desirable to test its accuracy. The first method that suggested itself was to carry out the entire determination on a sample of crude rubber to which a known amount of sulfur had been added in the form of some pure compound, such as sodium sulfate. Such experiments were carried out, but for another purpose, as will be explained later. It was believed, however, that the conditions of these experiments were not strictly comparable with those involved in the regular determination of sulfur in rubber, since in the latter case the sulfur is present partly in the free state and partly combined with rubber, whereas in the proposed test it would already be in the form of a soluble sulfate.

The only real test of any method is a comparison of the results obtained by it with those obtained by some method that is known to give reliable results. We have such a method in the well-known Carius procedure.

The chief objection to the Carius method is the fact that the sample generally used (0.15 to 0.20 gram) is small for an accurate determination of sulfur in rubber, particularly when the sulfur content is very small. It was found, however, that by using heavy Pyrex glass tubing (outside diameter 19 to 20 mm., thickness of wall 3 to 3.5 mm., and length 50 to 68 cm.) samples as large as 0.5 gram or slightly more could be used with 3.3 cc. of fuming nitric acid. Such tubes, originally about 68 cm. long, were used with such charges repeatedly, in some cases as many as ten to twelve times, until their length was reduced to 49 or 50 cm., without a single explosion.

It has been claimed that the Carius method gives high results due to the solvent action of the hot, fuming nitric acid on the glass. However, during the present investigation it was established that if both the inner and outer tubes, in which the sample is heated with the acid, are of Pyrex glass there is no danger of error from this source. This was determined by heating, in a sealed combustion tube of Pyrex glass, an empty sample tube, also of Pyrex glass (about 12 cm. long, 8 mm. in diameter, and weighing 7 to 10 grams), together with about two or three times the amount of fuming nitric acid used in an ordinary Carius determination. The heating (at 190° to 200° C.) was continued for 7 to 7.5 hours, whereas in an ordinary determination 3 hours were usually sufficient.

This was done four times, using three different tubes, one of the tubes being heated for a second period of 7 hours with a fresh portion of acid, so that it was thus treated for a total of 14 hours. In each case the inner tube was weighed both before and after heating, and in no case was a difference greater than 0.1 mg. noted. In two cases, also, the acid, after being thus heated in contact with Pyrex glass for 7 hours, was rinsed from the combustion tube and subjected to the usual treatment for the determination of sulfates; that is, it was evaporated to dryness, taken up with water, filtered, treated with barium chloride, filtered again, and the precipitate was then washed, burned, and weighed in the usual manner. In neither case was more than 0.1 mg. of precipitate obtained. All of these quantities are well within the limits of experimental error, and hence any errors due to solubility of the glass may be considered negligible. The Carius method was therefore adopted as a standard for testing the accuracy of the new method.

Some Faults of Kahane's Procedure and Their Correction

In attempting to follow Kahane's directions, however, some difficulties were encountered, and it was found desirable to modify the procedure in several details. In the first place, Kahane recommends the use of 10 cc. of 36° Bé. nitric acid and 5 cc. of 55° Bé. perchloric acid for a 1-gram sample of rubber. The nitric acid solution contains approximately 53 per cent of HNO_3 and can be obtained by mixing 2.16 volumes of concentrated nitric acid (sp. gr. 1.42) with 1 volume of water. This concentration, however, is too strong for those rubber samples which are finely divided or porous, as when crumbled on an ordinary compounding mill. The reaction then becomes so violent, even when the mixture is gently heated on a steam bath, that the flask becomes filled with a smoke consisting of fine particles of rubber, some of which are inevitably carried out of the flask. Better results were obtained by using more dilute nitric acid, such as is obtained by mixing equal volumes of the concentrated acid and water. Such a solution has a specific gravity of about 1.26, and contains approximately 41 per cent of HNO_3. With this concentration of acid the first step of the reaction—namely, the nitration of the rubber—may be accomplished easily and quickly by merely placing the flask containing the reacting materials on a steam bath. A 500 to 800 cc. Kjeldahl flask of Pyrex glass is recommended in place of the 250-cc. flask used by Kahane. When the nitration is completed, which usually requires only a minute or two and is indicated by the appearance of brown fumes and the subsidence of the reaction, some concentrated nitric acid may be added.

It is not desirable at this point, however, to heat the contents of the flask to active boiling, as recommended by Kahane, for, as will be shown later, such procedure will yield low results. The heating on the steam bath is therefore continued

for another 15 m' es or so until the rubber is nearly or entirely dissolved. The flask is then placed on a piece of asbestos gauze, with the neck of the flask inclined at an angle of about 45 degrees, and heated to gentle boiling over an ordinary burner. As the perchloric acid has little or no effect until the nitric acid is nearly or entirely boiled off, it need not be added until just before or even during this boiling operation. The introduction of a glass bead into the flask to prevent bumping is usually unnecessary. The heating is continued until white fumes fill the flask and the solution is clear and colorless or slightly yellowish. If the rubber compound being analyzed contains free carbon in any form it may be necessary to add more perchloric acid at this point, or if no other insoluble matter is present the carbon may be filtered off after cooling and diluting the solution.

It was also found that small amounts of nitric acid persist tenaciously in the final liquor, even after heating to dense white fumes. This nitric acid may be driven off completely by continuing the heating, but care should be taken not to drive off any of the sulfuric acid. Usually the nitric acid which remains after the organic matter is completely oxidized is negligible, but all traces of this acid can be removed without pushing the heating too far by allowing the liquid to cool somewhat after it has become clear, adding 5 cc. of concentrated hydrochloric acid, and again heating until white fumes appear.

Modified Procedure

The method in full, with the above modifications, as adopted for the writer's special purpose and as proposed for more general use, is as follows:

To a 1-gram sample of the finely divided or crumbled rubber in a 500–800 cc. Pyrex Kjeldahl flask (the larger size is preferable) add 10 cc. of a 41 per cent solution of nitric acid (1 volume concentrated acid and 1 volume water) and heat on a steam bath for 1 or 2 minutes until brown fumes appear and the reaction has subsided. Then add 10 cc. of concentrated nitric acid and continue heating for about 15 minutes more until rubber is nearly or entirely dissolved. Add 5 cc. of a 60 per cent solution of perchloric acid, set the flask in an inclined position on asbestos gauze, and heat with a burner to gentle boiling until dense white fumes appear and the solution (in absence of insoluble inorganic compounds) is clear and colorless or nearly so. At this point it may be necessary to add more perchloric acid (3 to 5 cc.) if free carbon is present, or, in absence of other precipitates, the carbon may be filtered off later. When all organic matter has been oxidized, allow to cool somewhat, add slowly 5 cc. of concentrated hydrochloric acid, and once more heat until white fumes appear, then allow to cool for a few minutes and wash into a beaker. If the solution is clear it may be heated at once (after diluting to about 200 cc.), treated with barium chloride, and the precipitate separated and weighed as barium sulfate in the usual manner. If the original free carbon of the rubber has not been completely oxidized, and it is known that no other insoluble matter is present, the carbon may be filtered off and the filtrate then treated for sulfates as before. If the liquor resulting from the oxidation of the rubber contains an

insoluble residue, and it is known to be solely barium sulfate, this may be filtered off, washed, ignited, and weighed as barium sulfate; or the insoluble residue, whatever its nature, may be filtered off, washed, dried, and fused with sodium carbonate, after which it is examined for sulfates, and possibly also for metals, according to the usual methods in such cases. (Sulfates may also be extracted from any insoluble residue by boiling with sodium carbonate, as will be described in a later paper on the decomposition of barium sulfate by solutions of sodium carbonate.[5]) In either event, however, the filtrate from such insoluble residue should always be treated for sulfates as above.

The method as thus outlined will require considerably more time for the oxidation of the sample than 7 or 8 minutes as claimed by Kahane; but no difficulty was experienced in completing the oxidation and (in absence of barium and lead) having the solution ready for treatment with barium chloride in 1.5 to 2 hours, which is still a considerable gain over the usual methods, besides requiring much less care and attention and avoiding some of the more objectionable operations which invite losses. Where highest accuracy is not required this period could be further shortened by eliminating the hydrochloric acid treatment without seriously affecting the final results.

Experiments and Results

COMPARISON OF PERCHLORATE AND CARIUS METHODS—Table I gives some results of analyses of a soft rubber compound by the method just described.

Table I—Analyses of Rubber by HClO Method

WEIGHT OF SAMPLE	WEIGHT OF $BaSO_4$	SULFUR
Grams	*Gram*	*Per cent*
1.1088	0.3433	4.25
1.4125	0.4375	4.25
1.2894	0.4011	4.27
1.4732	0.4581	4.27
1.1514	0.3567	4.25
1.2510	0.3908	4.29
	Av.	4.26

The same compound was then analyzed by the Carius method, using Pyrex glass tubing and approximately 0.5-gram samples with 3.3 cc. of fuming nitric acid. After opening each tube the solution was washed into a beaker, evaporated to dryness, treated with 5 cc. of concentrated hydrochloric acid, again evaporated to dryness, then taken up in water, acidified with 3 drops of concentrated hydrochloric acid, filtered, heated on the steam bath, and finally precipitated with a slight excess of barium chloride. The results are given in Table II.

Table II—Analyses of Rubber by Carius Method

WEIGHT OF SAMPLE	WEIGHT OF $BaSO_4$	SULFUR
Gram	*Gram*	*Per cent*
0.4897	0.1554	4.36
0.5062	0.1573	4.27
0.5012	0.1558	4.27
0.5070	0.1564	4.24
0.5115	0.1624	4.36
0.5095	0.1600	4.31
	Av.	4.30

[5] To appear in a subsequent issue.

The results by the Carius method are somewhat more erratic, but on the whole are slightly higher than those obtained by the perchloric acid method. This may be due in part to the fact that the samples used in the Carius method were smaller, and hence the percentage error would be greater, and partly to the fact that in the perchloric acid method the barium sulfate was precipitated in a more strongly acid medium and therefore was more soluble. When precipitated in the presence of 5 cc. of 60 per cent perchloric acid the barium sulfate came out of solution much more slowly than in a weakly acid solution, thus confirming the latter theory.

However, if we take the average of the Carius results as the true content of sulfur in this particular compound, we find that the average of the results obtained by the other method is only 0.04 per cent lower. This is not a very serious disagreement. At any rate we may fairly safely assume that, with such quantities of sulfur as are involved in the case under consideration, the perchloric acid method will get at least 99 per cent of the sulfur present.

Determination of Loss Due to Spray—In order to determine whether and to what extent any of the sulfur was lost during the boiling off of the nitric acid by being mechanically carried out of the flask in the form of spray, weighed quantities of pure, dry sodium sulfate were placed in Kjeldahl flasks together with 1.25 grams of crude rubber (pale crepe) in each case, treated with nitric and perchloric acids in the manner described above for the determination of sulfur, and finally precipitated with barium chloride. The amount of barium sulfate thus obtained was determined in the usual way, and the equivalent quantity of sodium sulfate, corrected for the sulfur present in the crude rubber and other reagents, was calculated therefrom. Table III shows these results as well as the ratio of the amount of sodium sulfate found to that taken in each case.

Table III—Comparison of Amounts of Sulfate Found to Those Taken

Na_2SO_4 Taken (*a*)	$BaSO_4$ Obtained (*b*)	Na_2SO_4 Found (*c*)	Ratio (*c*/*a*)
Gram	*Gram*	*Gram*	
0.2353	0.3877	0.2358	1.002
0.2055	0.3374	0.2053	0.999
0.2287	0.3738	0.2274	0.995
0.2656	0.4398	0.2677	1.008
		Av.	1.001

These results show that if the boiling is carried out slowly there will be no appreciable losses due to material being carried mechanically out of the flask.

Effect of Rapid Reaction—As already mentioned, Kahane claims that the oxidation of the rubber sample may be accomplished in 7 to 8 minutes. In order to determine the effect of very rapid reaction upon the analytical results, several determinations were made following the directions of Kahane as closely as possible except as to the concentration of the nitric acid, the size of the flasks, and the rate of boiling.

The same rubber was used as for the results given in Tables I and II.

Samples of this rubber, weighing approximately 1 gram each, were placed in 800-cc. Kjeldahl flasks, treated with 15 cc. of a 1:1 solution (approximately 41 per cent) of nitric acid and 5 cc. of a 60 per cent solution of perchloric acid, placed on asbestos gauze, warmed gently at first until the nitration was completed, then heated to active boiling until dense white fumes filled the flask. The boiling was pushed as rapidly as was deemed practicable, and still the oxidation was not completed in anything like 7 to 8 minutes; the periods actually required ranged from 18 to 22 minutes.

The results obtained in this series of experiments are shown in Table IV. In the first three determinations no glass beads were used and there was frequent violent bumping. In the last three a bead of Pyrex glass about the size of a small pea was placed in each flask, and the boiling was active but smooth and regular, with practically no bumping or spurting. In all cases, however, when the nitric acid was practically all boiled off and white fumes began to appear, a violent reaction took place producing a violent effervescence in the liquid. It is probably this effervescence that is responsible for a large part of the loss. This violent reaction is not observed when the rubber is allowed to dissolve slowly on the steam bath followed by gentle boiling for an hour or so, because during the slower digestion most of the organic matter is destroyed by the nitric acid and less of it remains to react with the perchloric acid when the solution becomes concentrated.

Table IV—Influence of "Active" Boiling

Weight of Sample	Weight of $BaSO_4$	Sulfur	Loss[a]
Grams	*Gram*	*Per cent*	*Per cent*
1.0764	0.3225	4.11	4.5
1.0213	0.3064	4.12	4.2
1.0047	0.2994	4.09	4.9
1.0527	0.2981	3.89	9.5
1.0232	0.3024	4.06	5.6
1.0372	0.3037	4.02	6.5

[a] Based on average of Table II.

The reaction was possibly more violent in the last three determinations in Table IV, owing to more vigorous heating, which may account for the somewhat higher losses. All the results, however, are considerably below those shown in Tables I and II, indicating clearly that too rapid boiling must be avoided if accurate results are desired. In these last three determinations 5 cc. of concentrated hydrochloric acid were added to the flask after the oxidation was completed, and heating was resumed until white fumes once more appeared, in order to destroy any residual nitric acid which might still be present. In at least one of these cases the presence of such traces of nitric acid was clearly indicated by the appearance of brown fumes upon the addition of the hydrochloric acid.

Effect of Perchloric Acid on Occlusions by Precipitate—Since the solution obtained in this method of oxi-

dizing the rubber always contains more or less perchloric acid, in the presence of which the barium sulfate must be subsequently precipitated (unless the acid is neutralized, which is objectionable), it was considered desirable to determine the influence of perchloric acid upon occlusions by the precipitate.

Table V—Barium Sulfate Precipitated in Presence of Various Acids

(Theoretical weight of $BaSO_4$ = 0.5205 gram)

From H_2SO_4 Alone	In Presence of 5 cc. Concd. HCl	In Presence of 5 cc. 60% $HClO_4$
Gram	*Gram*	*Gram*
0.5214	0.5215	0.5214
0.5207	0.5222	0.5248
0.5189	0.5227	0.5204
0.5211	0.5239	0.5208
Av. 0.5205	0.5226	0.5218

A standard solution of sulfuric acid was prepared, which by titration was found to contain 0.2188 gram of sulfuric acid (equivalent to 0.5205 gram of barium sulfate) per 100 cc. From this solution twelve equal portions of 100 cc. each were measured out into separate beakers by means of the same 100-cc. pipet, and divided into three groups of four samples in each group. To the first group no other acid was added, but to the second group were added 5 cc. of concentrated hydrochloric acid, and to the third 5 cc. of 60 per cent perchloric acid in each case. Each was then diluted with distilled water to a volume of 200 cc., heated on the steam bath, and finally precipitated by means of a solution of barium chloride containing 0.1 gram of the anhydrous salt per cubic centimeter. To the first series of samples only 5 cc. of this barium chloride solution were added, this being an excess of only about 7.3 per cent over the amount theoretically required, in order that occlusion of barium chloride would be reduced to a minimum. But in the other series 7 cc. of the barium chloride solution were used in each case in order to simulate more nearly the conditions of ordinary analytical practice in which the exact amount of barium chloride required would not be known, and hence an excess would have to be added. After standing overnight (about 20 hours) all the precipitates were filtered off, washed, ignited, and weighed in the usual way. The results are given in Table V.

The average of the first series agrees with the theoretical result based upon ordinary acidimetric titration. In the second column we have confirmation of the well known fact that hydrochloric acid has a marked influence on the occlusion of barium chloride by barium sulfate precipitates. In the third series, although the average is also somewhat above the theoretical, it is not so high as that in the second column; and on examining the individual results in this column we find that the high average is due almost entirely to the second member of the series, the others being very close to the average of the first series. Furthermore, it must be remembered

that in this case we have the full amount of perchloric acid that will ordinarily be used in an actual analysis (5 cc.), a large part of which will be destroyed or volatilized in the course of such determination. Hence it may be safely concluded that any unchanged perchloric acid which may remain after the oxidation of the rubber sample in the course of regular analytical work will have only a negligible influence upon the result.

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Inaccuracies in Determination of Acidity of Raw Rubber by Water Extraction[1]

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DURING the course of an investigation on ultra-accelerators the basic rubber–sulfur–zinc oxide mix used for curing experiments showed a maximum tensile of 126.5 kg. per sq. cm. A mix of rubber 100, sulfur 10, with no zinc oxide, showed a tensile of less than 84.5 kg. per sq. cm. This was so low that it seemed desirable to investigate further. The first hypothesis was that the increase in tensile brought about by zinc oxide was due, not only to the reënforcing effect of the pigment, but also to the neutralization of excess acid in the smoked sheet.

To determine the water-soluble acids in rubber a common method has been to extract the rubber with hot water in much the same manner as the conventional acetone extraction. This was done with the rubber in question, but failure to obtain consistent values for acid numbers led to a critical examination of the method and the conclusion that hydrolysis of esters in the rubber by the hot water can take place. The result is a very high value for water-soluble acids. To avoid all trouble, it is best to employ the procedure used by Van Rossem and Dekker[2] where the rubber is first extracted

[1] Presented under the title "Determination of Acidity of Raw Rubber by Water Extraction" before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

[2] Ind. Eng. Chem., **18**, 1152 (1926).

with acetone and the acetone extract then digested with water at low temperature to determine water-soluble acids.

Experimental

Three samples of the smoked sheet were extracted for 8 hours with hot water and then for 8 hours with acetone. The acid numbers[3] obtained are shown in Table I.

Table I—Acid Numbers of Water and Acetone Extracts

	Sample I	Sample II	Sample III
Water extract	291 (*M*)	130 (*M*)	273 (*M*)
Acetone extract	292 (*N*)	292 (*N*)	289 (*N*)

These results indicated an unusually high acid content of the rubber. However, the one low value (130) caused suspicion. The three samples having been extracted at the same time, there seemed to be no explanation for this failure to get check results. To test the method, a specimen of first latex crepe was selected and water extraction of samples cut from this was carried out. The acid numbers varied from 50 to 175 on six samples. From this it appeared that something more than simple extraction of water-soluble acids was taking place. In the hope of finding plausible explanation for this condition the procedure outlined by Van Rossem and Dekker was carried out. In this process the rubber is first extracted with acetone; water-soluble acids are then determined by water extraction of this acetone extract on a water bath until further extraction shows no increase in acidity.

Table II—Acid Numbers by Van Rossem and Dekker's Method

A + *B*—Total acid number of acetone extract
A—Water-soluble free fatty acids (water extraction of acetone extract at temperature of water bath)
B—Liquid and solid free fatty acids (acetone-soluble only)
SS-1—Smoked sheet used in mixes giving low tensile
SS-2—Smoked sheet known to give good tensile properties in a rubber-sulfur mix

				Acetone Extract after *A* Boiled with Water:		Acetone Extract Boiled 16 Hours with Water
	A + *B*	*A*	*B*	8 hours	6 hours more	
SS-1	342	53[a]	289[a]			
SS-1 (extract air - dried 1 month)	273	60				187
SS-2	248	42 (*X*)	206	64	33	
	Water extraction first (16 hours)			Acetone extraction following		
SS-2	489	399[c]			238[b]	

[a] Compare values (*M*) Table I. [b] Compare values (*N*) Table I.
[c] Compare value (*X*) above.

Colored solutions were titrated electrometrically. Some titrations were made with alcoholic potassium hydroxide standardized against pure stearic acid. Water solutions were referred to sodium carbonate as ultimate standard. All solutions were cross-checked to eliminate possible errors. In all cases duplicate acid numbers checked satisfactorily within the limits of experimental error. The average results are shown in Table II.

[3] Whitby and Winn, *J. Soc. Chem. Ind.*, **42**, 336T (1923); Whitby, *Trans. Inst. Rubber Ind.*, **1**, 12 (1925); Whitby and Greenberg, Ind. Eng. Chem., **18**, 1168 (1926).

This shows that boiling the acetone extract with water increases the acid number. It seemed as if a similar effect ought to be noted on very long heating with water on the steam bath. On testing this, the results in Table III were obtained.

Table III—Effect of Long Heating with Water

		Acid Number
A	Water extraction of acetone extract SS-1	53
C	Extracted 12 hours on boiling water bath	53
D	Residue from *C* boiled with water 6 hours	97

Discussion

The value *A* in Table II for SS-1 should agree with *M* in Table I, as both are supposed to be measures of water-soluble acids only. Value *B* (Table II, SS-1) agrees with *N* (Table I) as it should, because both measure acetone-soluble acids only. In the case of SS-2 in Table II, the value *A* (42) should equal the values (489, 399) obtained by direct water extraction if nothing is happening except simple extraction. To determine whether a similar effect could be noted in extracting an acetone extract with water, several acetone extracts were boiled with water as indicated. In every case the acid numbers increase with time of boiling. However, as Table III shows, the water must be near the boiling point, for no effect on the acidity was noted by heating a fresh acetone extract with water for 12 hours on a water bath, but the residue from this water extraction gave an increase in acid number of 97 when boiled with water.

Conclusion

From the results obtained it is concluded that the boiling water hydrolyzes some of the esters in the acetone extract. In the case of direct extraction of the rubber with water, hydrolysis of esters must take place in the rubber, forming water-soluble acids; or else, although the esters are practically insoluble in the water, it extracts a little ester each time the extraction thimble empties (Bailey-Walker apparatus), carrying the ester down to be hydrolyzed in the boiling water below. Temperature and time of heating play a prominent part. The temperature must be close to the boiling point and the acidity increases progressively with time of heating. The fact that temperature is so important in producing this effect accounts for the erratic values obtained by direct water extraction. On the electric hot plates used water did not always boil steadily, and that contained in the thimble might vary considerably in temperature, much of the time not being hot enough to hydrolyze or extract any ester.

Therefore, to avoid any difficulty in the determination of water-soluble acids in rubber, extract first with acetone, then digest this extract with water on a boiling water bath until no increase in acidity of the water extract is obtained. This is a part of the procedure developed at the Netherlands Government Institute by Van Rossem and Dekker.

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Some Observations with Ultra-Accelerators[1]

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ALTHOUGH much has been done on accelerators, in such a vast field there is always room for additional work, particularly if, as Whitby predicts,[2] ultra-accelerators will be the main class used in course of time. This investigation was started with the following points in view: (1) to prepare several thiuramdisulfides and related compounds; (2) to note their relative behavior when used as accelerators; and, if possible, deduce some explanation for the mode of action of the class or for the behavior of some particular compound, or gain additional evidence for any existing theories.

The relative inactivity of thiurams derived from primary amines has been mentioned[3,4] but no explanation published. Evidence is presented to show that decomposition of the compound into hydrogen sulfide and a mustard oil takes place so quickly at the temperatures used that there is not time for the generation of much active accelerator.

It was found that tetramethylthiurammonosulfide plus sulfur equivalent to the difference in sulfur content between it and the disulfide gave a cure in a rubber–zinc oxide mix practically equivalent to that given by the disulfide alone. This indicates that zinc dimethyldithiocarbamate may be the active accelerating agent.

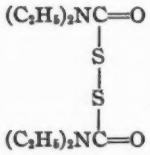
[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

[2] IND. ENG. CHEM., **15**, 1005 (1923).

[3] Romani, *Giorn. chim. ind. applicata*, **3**, 197 (1921); *C. A.*, **16**, 854 (1922).

[4] Twiss, Brazier, and Thomas, *J. Soc. Chem. Ind.*, **41**, 81T (1922).

Romani[5] has noted that replacement of one of the sulfur atoms of the -CSSH group of dithio acids by an oxygen atom destroys the accelerating power. The action of carbon oxysulfide on diethylamine gave a compound whose zinc salt did act as an accelerator in a rubber–sulfur–zinc oxide mix; but it was very slow, showing that the above observation is applicable also to the carbamates. Oxidation of the diethylaminediethylmonothiocarbamate yielded an oil which decomposed so readily that it seemed unnecessary to test it as an accelerator. No analysis was made, but the decomposition products indicated that the compound was the one desired—namely,



Curing experiments were carried out with the thiuramdisulfides and dithiocarbamates. The compounds derived from an ethylamine seem to be a little more rapid in bringing about maximum tensile strength. With the rubber used, increase in tensile attributable to the effect of the accelerator amounts to about 100 per cent. The accelerator also speeds up aging to some extent, but this can be easily overcome by the use of a small quantity of antioxidant.

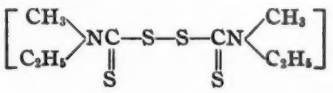
Preparation of Compounds

In the preparation of all thiuramdisulfides the method given by Braun[6] was followed generally, such modifications in temperature control as seemed advisable being introduced. This consists in treating an ice-cooled alcoholic solution of 2 mols amine and 1 mol carbon disulfide with an alcoholic solution of 1 mol iodine to oxidize the intermediate dithiocarbamate. The disulfide separates soon or on addition of ice water. This procedure was followed exactly in the preparation of the tetramethyl, dimethyldiethyl, and dimethylthiurams. In the case of the tetraethyl and dimethyldiphenyl compounds the separation of the thiuram can be hastened by warming the mixture after the iodine has been added. The dimethyldiphenylthiuramdisulfide was rather impure at first and was recrystallized from a mixture of alcohol and chloroform. The oxidizing agent used throughout these experiments was a saturated alcoholic solution of iodine, which proved to be very convenient as well as to give good results, although Romani,[5] referring to tetramethylthiuramdisulfide, states that the quickest way is to pass chlorine through an aqueous solution of the corresponding dithiocarbamate. No reference to a thiuram made from

[5] *Caoutchouc*, **19**, 11626 (1922); *C. A.*, **17**, 901 (1923).

[6] *Ber.*, **35**, 817 (1902).

an amine containing two different alkyl groups was found in the literature. Consequently, one was prepared from methylethylamine in order to yield symmetrical dimethyldiethylthiuramdisulfide:



Determination of sulfur showed 47.62 per cent (theoretical 47.78 per cent).

Tetramethylthiuram monosulfide was made from the disulfide by warming with potassium cyanide in dilute alcohol.[7]

Zinc salts of the dithiocarbamates were obtained by treatment of the carbamates in solution with zinc acetate.

To test the effect of a -COSH group, carbon oxysulfide, prepared from ammonium thiocyanate and sulfuric acid,[8,9,10] was passed through a cold alcoholic solution of diethylamine.

Melting Points of Thiurams Prepared

	Found	Recorded Previously
Tetramethylthiuram disulfide	146° C.	146[8]
Tetraethylthiuram disulfide	69.5–70	70[8]
Dimethylthiuram disulfide	101.5–102	102[8]
Dimethyldiphenylthiuram disulfide	192	198[8]
Dimethyldiethylthiuram disulfide	72	...
Tetramethylthiuram monosulfide	105–106	106[7]

Dimethylthiuramdisulfide Inactive

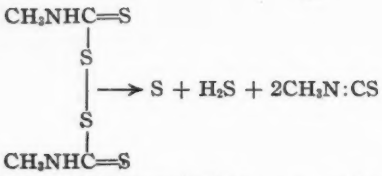
When milled into rubber in the same relative proportion as the other thiurams, the dimethylthiuram disulfide showed almost no activity, whereas the tetramethyl derivative exhibited high accelerating power. This observation is similar to that made by Romani,[3] Twiss,[4] and others. Twiss states that the easy conversion of the dithiocarbamates of primary amines into mustard oils of unpleasant odor has been given as an objection to their use, and says, "The dialkylamine derivatives are likely to prove preferable on more weighty grounds; they are clearly much more effective." The lack of activity in the corresponding thiurams also "indicates a fundamental difference between the behavior of the primary and secondary amine derivatives." One would naturally make the deduction that the lack of activity and easy decomposition might be closely connected. Dimethylthiuramdisulfide was heated on the steam bath and in an air bath, alone; mixed with sulfur and zinc oxide; and mixed with sulfur, zinc oxide, and rubber. In all cases hydrogen sulfide and mustard oil vapors were evolved. Hence it can be concluded the reaction

[7] Braun and Stechele, *Ber.*, **36**, 2275 (1903).

[8] Beilstein, I, p. 877.

[9] Fischer, *Biochem. Z.*, **125**, 12 (1921); *C. A.*, **16**, 964 (1922).

[10] Schmidt, *Ber.*, **10**, 191 (1877).



Dimethylthiuramdisulfide ⟶ sulfur + hydrogen sulfide + methyl isothiocyanate

proceeds so rapidly that there is very little chance for any cyclical set of changes activating the sulfur and regenerating the activating agent to take place before the thiuram is all destroyed by the irreversible decomposition.[11] Furthermore, after standing several weeks the thiuram no longer showed a melting point of 102° C. This was anticipated from the fact that it decomposed on the steam bath. It began to decompose and finally liquefied at about 95° C. Also, a piece of lead acetate paper suspended in the container showed unmistakable evidence of hydrogen sulfide in half an hour at room temperature.

Table I—Curing Data: Basic Mix Plus 1/1200 Mol Thiuram Disulfide

(A) Tetramethylthiuramdisulfide (C) Dimethyldiethylthiuramdisulfide
(B) Tetraethylthiuramdisulfide (D) Dimethyldiphenylthiuramdisulfide

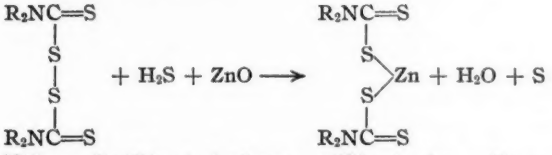
	(A)		(B)		(C)		(D)	
	Lbs./ in.²	*Kg./ cm.²*	*Lbs./ in.²*	*Kg./ cm.²*	*Lbs./ in.²*	*Kg./ cm.²*	*Lbs./ in.²*	*Kg./ cm.²*
				30-MINUTE CURE				
T_3	231	16.2	200	14.05	163	11.4	238	16.7
T_5	770	54.1	645	45.3	727	51.1	824	57.8
T_B	3230	226.7	3330	233.7	3600	253.1	3190	224.0
E_B	720%		760%		730%		712%	
T.P.	2325	163.45	2530	177.6	2630	184.5	2270	159.5
				35-MINUTE CURE				
T_3	257	18.05	214	15.02	175	12.3	240	16.9
T_5	956	67.1	734	51.6	863	60.6	840	59.0
T_B	3910	275.0	3610	254.0	3650	256.1	3288	232.5
E_B	725%		750%		717%		709%	
T.P.	2835	198.5	2710	190.5	2615	184.0	2335	164.0
				40-MINUTE CURE				
T_3	296	20.8	276	19.4	261	18.35	287	20.2
T_5	1013	71.2	902	63.3	1095	77.0	975	68.5
T_B	3040	213.5	3684	258.5	3490	245.0	3285	230.5
E_B	672%		709%		675%		690%	
T.P.	2045	143.8	2610	183.5	2350	165.2	2270	159.5
				45-MINUTE CURE				
T_3	294	20.6	245	17.3			283	19.9
T_5	1025	72.06	965	67.8			1067	75.0
T_B	3363	236.5	3630	255.0			3367	236.5
E_B	690%		702%				679%	
T.P.	2320	163.0	2025	142.36			2290	161.0

When tetramethylthiuramdisulfide is heated with rubber, sulfur, and zinc oxide in an air bath, no hydrogen sulfide is evolved at first, but the vapors are alkaline. Soon, as the temperature rises, hydrogen sulfide begins to escape and the alkalinity increases. After a short time the alkaline vapors cease. The presence of these vapors is easily explained by the mechanism suggested by Bedford and Sebrell[12] and Bed-

[11] Compare Twiss and Thomas, *J. Soc. Chem. Ind.*, **42**, 899T (1923), referring to xanthates.

[12] J. Ind. Eng. Chem., **14**, 25 (1922).

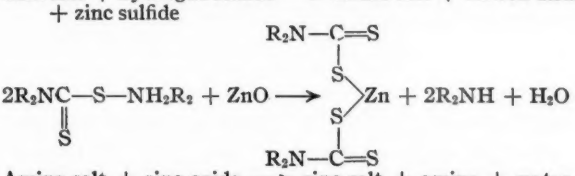
ford and Gray[13] for the action of zinc oxide and hydrogen sulfide, coming from the union of rubber and sulfur, on thiuramdisulfides. The fact that the alkaline vapors do not continue may be explained either by supposing that the thiuram has all reacted or decomposed and hence does not generate any more amine (or other alkaline product), or that the carbon disulfide formed reacts rapidly enough with the amine to prevent the escape of the latter. In view of the high accelerating power of the disulfide, the second reaction must preponderate, at least in the curing mold. The following summary, given by Bedford and his co-workers, shows the reactions possible:



Thiuramdisulfide + hydrogen sulfide + zinc oxide ⟶ zinc dialkyl dithiocarbamate + water + sulfur

$(R_2N—CS—S)_2Zn + H_2S \longrightarrow R_2NCS—S—NH_2R_2 + CS_2 + ZnS$

Zinc salt + hydrogen sulfide ⟶ amine salt + carbon disulfide + zinc sulfide



Amine salt + zinc oxide ⟶ zinc salt + amine + water

$2R_2NH + 2CS_2 + ZnO \longrightarrow (R_2N—CS—S)_2Zn + H_2O$

Amine + carbon disulfide + zinc oxide ⟶ zinc salt + water

Research having in view isolation of reaction products of the accelerators during vulcanization should throw much light on the mode of action of these bodies.

Thiuramdisulfide *vs.* Monosulfide Plus Sulfur

It is well known that tetramethylthiuramdisulfide will cure without sulfur quite readily, whereas the corresponding monosulfide will cure only very slowly under similar conditions. Two batches were made up as follows:

Formula I		Formula II	
Rubber	200	Rubber	200
Zinc oxide	10	Zinc oxide	10
Disulfide	10	Monosulfide	8.666
		Sulfur	1.334

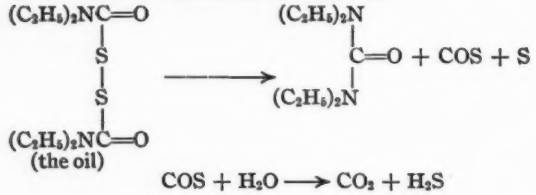
The sulfur used in II is equivalent to the difference in sulfur content between monosulfide and disulfide. A 1-hour cure of these mixes was too soft to remove from the mold. Substantially equal cures were obtained from both mixes in 2, 3, 4, and 5 hours at 115° C., indicating that in curing with the monosulfide, sulfur, and zinc oxide the same substance is

[13] *Ind.* Eng. Chem., **15**, 720 (1923).

formed as is produced from zinc oxide and the disulfide, this substance in turn being the active agent in promoting vulcanization. This substance would be expected to be zinc dimethyldithiocarbamate, thus adding another bit of evidence to the contention of Bedford and others that the zinc salts are the active agents in causing acceleration when using dithiocarbamates or thiuramdisulfides. In one trial monosulfide was heated in an open crucible with sulfur and with sulfur and zinc oxide. No substances having the melting point of tetramethylthiuramdisulfide or zinc dimethyldithiocarbamate were obtained. While this does not confirm the above hypothesis concerning the behavior of monosulfide with sulfur and zinc oxide, it does not in any way disprove it.

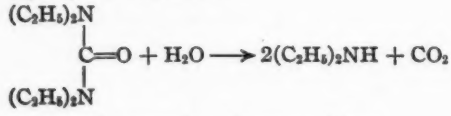
Monothiocarbamates and Their Oxidation Products

When carbonyl sulfide was passed into diethylamine well cooled in a mixture of ice and salt, a solid was formed which is in all probability diethylamine-diethylmonothiocarbamate. A portion of this was dissolved in water and treated with iodine. When no more iodine was taken up, the resulting liquid was evaporated with a current of air, yielding an oil. Another portion in water solution gave a sticky precipitate when zinc acetate was added. This precipitate was dried and found to have some accelerating power, $^1/_{1200}$ mol (assuming it to be zinc diethylmonothiocarbamate) producing a cure in 4 hours at 115° C. in the standard mix used throughout this work. More of the oil mentioned above was prepared and extracted with ether. The aqueous layer yielded diethylammonium iodide. The ether was allowed to evaporate and the oil left several weeks at room temperature. After a few days some sulfur separated out accompanied by a slight evolution of hydrogen sulfide. This continued steadily but slowly. Addition of concentrated hydrochloric acid gave much hydrogen sulfide and sulfur. Boiling and subsequent neutralization of the acid solution showed the presence of diethyl amine. The mechanism of the spontaneous decomposition may be represented as follows:

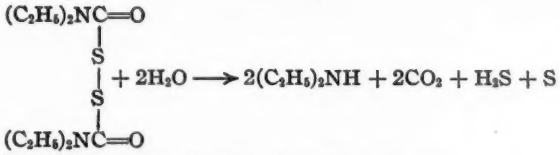


$$COS + H_2O \longrightarrow CO_2 + H_2S$$

In the presence of hydrochloric acid the reactions proceed rapidly and further:



making the complete decomposition:



Tetraethyluraminedisulfide + water ⟶
diethylamine + carbon dioxide + hydrogen sulfide + sulfur

This oil was not tested as an accelerator, but since it is unstable at room temperature, decomposition would probably prevent it from showing much power. With zinc oxide it should form a salt equivalent in activity to the zinc salt prepared. This salt shows decomposition without melting, which is not true of any of the zinc dialkyldithiocarbamates or the corresponding thiuramdisulfides which were investigated. Before many definite conclusions are drawn regarding the accelerating value of the uraminedisulfides, however, more work should be done; but the above is a possible explanation of the fact that replacing one sulfur atom in the -CSSH group by oxygen removes the activity as an accelerator.

Table II—Curing Data: Basic Mix Plus 1/1200 Mol Dithiocarbamate

(E) Zinc dimethyldithiocarbamate
(F) Zinc diethyldithiocarbamate

	(E)		(F)	
	Lbs./in.²	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*
		25-MINUTE CURE		
T_3			226	15.8
T_5			818	57.5
T_B			3510	247.0
E_B			711 %	
T.P.			2490	175.0
		30-MINUTE CURE		
T_3	279	19.6	275	19.3
T_5	914	64.2	886	62.3
T_B	3090	217.0	3370	237.0
E_B	674%		712%	
T.P.	2085	146.5	2400	168.74
		35-MINUTE CURE		
T_3	288	20.2	269	18.9
T_5	935	65.6	982	69.0
T_B	3190	224.0	2810	197.0
E_B	677%		668%	
T.P.	2160	151.8	1880	132.0
		40-MINUTE CURE		
T_3	292	20.5		
T_5	988	69.4		
T_B	2980	209.5		
E_B	664%			
T.P.	1980	139.2		

Curing Experiments

The rubber used for all curing experiments was a good grade of ribbed smoked sheet which had been previously masticated in 100-pound lots on an 80-inch mill. The basic mix consisted of rubber 100, zinc oxide 5, sulfur 10, and gave a maximum tensile of 126.5 grams per sq. cm. (1800 lbs. per sq. in.) To this was added $^1/_{1200}$ mol of ultra-accelerator. The rubber was broken down for 15 minutes on a 12-inch (30-cm.) experimental mill cooling the rolls with a slow stream of water. The compounding ingredients were added and

Table III—Aging Data

	Before Aging		1 Day		2 Days		3 Days		4 Days		5 Days		6 Days		7 Days	
	Kg./cm.²	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*	*Kg./cm.²*	*Lbs./in.²*
	(A) BASIC MIX PLUS 1/1200 MOL TETRAMETHYLTHIURAM DISULFIDE															
T_3	19.3	275	24.7	351	25.1	357										
T_5	64.3	914	97.0	1380	92.5	1317										
T_B	242	3440	249.59	3550	164.5	2340					11.7	167	13.9	198	9.6	137
E_B	700%		670%		588%						175%		250%		200%	
T.P.	169	2410	167	2380	96.66	1375					2.06	29.3	3.48	49.5	1.92	27.35
	(B) BASIC MIX PLUS 1/1200 MOL ZINC DIMETHYLDITHIOCARBAMATE															
T_3	14.05	200	23.3	332	23.8	339										
T_5	58.00	825	103.69	1475												
T_B	204	2910	220	3135	79.4	1130	23.4	334					9.26	132	14.6	208
E_B	668%		640%		475%		295%						190%		212%	
T.P.	137	1945	140.62	2001	37.8	538	6.82	98.6					1.79	25.5	3.09	44.0
	(C) BASIC MIX CURED 150 MINUTES AT 141° C.															
T_3	6.8	96.7					9.48	135	17.0	242						
T_5	15.7	224														
T_B	99.7	1420					53.4	760	27.6	393	11.4	163				
E_B	810%						475%		370%		337%					
T.P.	80.85	1150					25.4	361	10.2	145.5	3.88	55.2				
	(D) SAME AS (A) BUT RUN PARALLEL WITH (E)															
T_3	13.6	194	18.7	266	20.3	289										
T_5	54.50	777	20.8	1009	82.8	1178										
T_B	256.62	3650	128.5	1830	88.2	1255					12.3	176	13.6	194	11.2	160
E_B	768%		575%		525%						205%		225%		195%	
T.P.	197.5	2810	73.82	1051	46.3	659					2.54	36.2	3.65	43.7	2.19	31.2
	(E) (A) PLUS 1 PART ANTIOXIDANT															
T_3	14.7	209	21.7	309	21.4	305					25.2	359	21.8	310	23.6	336
T_5	54.7	780	87.5	1245	90.7	1290					99.7	1420	91.90	1300	100.2	1428
T_B	234.5	3340	287.5	4090	256.62	3650					149.0	2120	155.5	2215	165.8	2360
E_B	722%		727%		695%						550%		575%		580%	
T.P.	169.0	2410	209.12	2975	178.5	2540					81.4	1157	89.63	1275	96.4	1370

milling was completed in 5 minutes. Curing was done in a two-platen press whose temperature was checked by a Bristol recording thermometer which had been standardized against a mercury thermometer placed between the platens. The mold had two chromium-plated cavities approximately 0.1 inch (2.5 mm.) deep and of sufficient size to allow four dumb-bell test pieces to be cut from each slab. The die used had a constriction 2 inches long and 0.25 inch (6 mm.) wide. Tensile tests were made on a Scott vertical tester equipped with a recording device. In the accompanying tables, the ultimate tensile strength is represented by T_B, the load at an elongation of x00 per cent by T_X, and the elongation at break by E_B. T. P. indicates the tensile product $(E_B \times T_B)/1000$.

While no striking differences between these accelerators are shown, those derived from an ethylamine appear to be somewhat more rapid.[4] Among the thiuramdisulfides there is a distinct tendency toward discontinuity of vulcanization even with the 5 parts zinc oxide. Had longer cures been made with the dithiocarbamates, doubtless the same effect would have been observed.[14] The dithiocarbamates are more rapid than the corresponding thiurams.

Aging

The aging tests were carried out in an electric oven at 70° C. After removing from the oven, strips were allowed to remain at about 20° C. for 24 hours before testing. The initial results with tetramethylthiuramdisulfide showed such very poor aging qualities that it seemed advisable to compare the behavior of the basic mix even though the curing had to be done at a higher temperature.

The aging qualities of the rubber used are evidently very poor, but nevertheless the accelerator speeds up the effect of aging some. All the accelerated samples except (D) show distinct after-curing. There is also a discontinuity of aging noticeable. This may have no meaning, being due simply to a slight lack of uniformity in the test pieces; but since it occurs in every case among the accelerated stocks, it is more probable that it may represent a change in state of aggregation of the rubber or in some other factors affecting vulcanization. The same factor which causes discontinuity of vulcanization may bring about this effect during aging. The efficiency of the antioxidant is great.

Acknowledgment

The authors wish to express their gratitude to members of the Chemistry Department of the University of Akron for their help and to R. P. Dinsmore and L. B. Sebrell, of the Goodyear Tire and Rubber Company, for comments and suggestions on the organization of this paper.

[14] Twiss. *J. Soc. Chem. Ind.*, **40**, 242T (1921).

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Accurate Method for Comparison of Scorching Qualities of Accelerators[1]

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MILLER RUBBER CO., AKRON, OHIO

PRACTICAL experience has shown that there is a wide difference in the behavior of accelerators when used on a commercial scale. Some accelerators give stocks that are free from scorching or "set up" in mill practice, while others require special equipment if they are to be handled without causing an undue amount of prematurely cured stock, and still others give stocks that cannot be handled commercially at all.

Methods of Determining Scorching

The literature gives numerous citations dealing with scorching or burning tendencies of accelerators, but detailed methods of measuring this tendency to vulcanize prematurely are meager. It is a matter of common knowledge, however, that five methods of determining scorching are, or have been, in vogue.

(1) One very common method consists of making various cures on the stock containing the accelerator to be studied, over a considerable period of undercure and at different steam pressures, then judging that accelerator which gives the highest

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

tensile strength on the undercured branch of the time-tensile curve to be the most difficult to handle.

(2) Another method carries out the study of the materials on the mill at elevated temperatures. The mill rolls are heated and the stock is milled under this condition until scorching becomes apparent.

(3) A third method consists of introducing the uncured stock into an extruding instrument at a certain temperature, and, after a given time, extruding under constant pressure.[2] The amount extruded in an interval of time is measured or weighed. As the stock sets up less will be extruded, and by comparing the amounts extruded an idea is obtained of the scorching tendencies of the accelerators.

(4) Another method is to make plasticity measurements with a Williams plastometer after the stock has been exposed to a certain temperature for a definite period of time.[3]

(5) Still another method consists in curing a cement film containing the accelerator at 70° C. in carbon dioxide and determining the time of set up by stretching the film with the fingers.[4]

These above procedures are open to several objections. That of measuring set up by the position of the undercured portion of the time-tensile curve is poor practice because it leads to erroneous conclusions, as will be shown later. Milling at elevated temperatures brings in the problems of accurate control of temperature on the mill, differences in plasticity caused by the accelerators themselves, difficulty of duplicating results, and usually the measurement is made above the operating temperature of the normal stock, which might lead to the same erroneous conclusions as the time-tensile curve method of judging set up. The use of the Marzetti extruder is exceedingly cumbersome and time consuming and subject to the differences in plasticity of raw stocks caused by different accelerators. The Williams plastometer measurements are also subject to the latter objection. Both methods are very sensitive to differences in milling. The examination of the cure by stretching the film with the fingers is an approximate at best and is subject to the personal equation. It does not give definite figures or enable one to follow the set up curve accurately.

The purpose of this paper is to describe a visual method of measuring the set up curve, which is designed to overcome, to a large extent, the objections to existing methods, and has been found to be of practical use in evaluating a number of accelerators.

Method and Apparatus

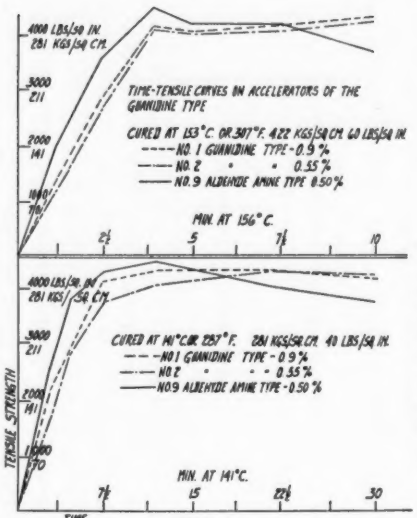
It is well known that when a thoroughly milled uncured rubber compound is immersed in a solvent the rubber and the filler, or pigment, are dispersed throughout the solvent. This dispersion of pigment is complete in the case of zinc oxide.[5] It is highly desirable in the determination of set up, or the

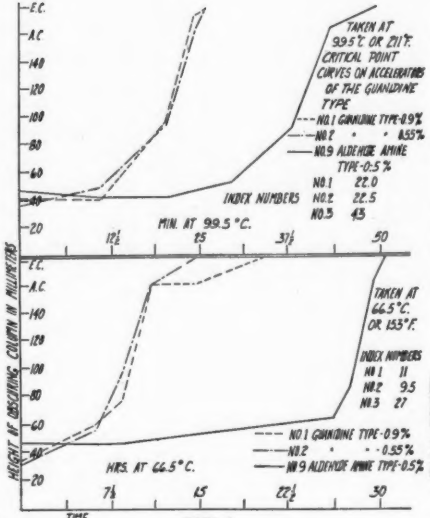
[2] Marzetti, *Giorn. chim. ind. applicata*, **5**, 342 (1923); *C. A.*, **17**, 3628 (1923).

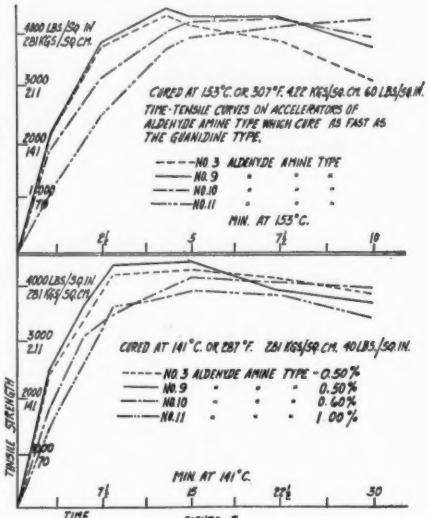
[3] Krall, IND. ENG. CHEM., **16**, 922 (1924).

[4] Cadwell and Smith, *India Rubber World*, **68**, 782 (1923).

[5] Stamburger, *Kolloid-Z.*, **42**, 295 (1927).


4000 LBS/SQ IN.
281 KGS/SQ CM.
3000
211
2000
141
1000
70
TIME-TENSILE CURVES ON ACCELERATORS OF THE GUANIDINE TYPE
CURED AT 153°C. OR 307°F. 4.22 KGS/SQ CM. 60 LBS/SQ IN.
NO. 1 GUANIDINE TYPE - 0.9 %
NO. 2 " " 0.55 %
NO. 9 ALDEHYDE AMINE TYPE 0.50 %
MIN. AT 156° C.
2½
5
7½
10
CURED AT 141°C. OR 287°F. 281 KGS/SQ CM. 40 LBS/SQ IN.
NO. 1 GUANIDINE TYPE - 0.9 %
NO. 2 " " 0.55 %
NO. 9 ALDEHYDE AMINE TYPE - 0.50 %
MIN. AT 141°C.
7½
15
22½
30
TENSILE STRENGTH
TIME
FIGURE 1.


E.C.
A.C.
140
120
100
80
60
40
20
TAKEN AT 99.5°C. OR 211°F.
CRITICAL POINT CURVES ON ACCELERATORS OF THE GUANIDINE TYPE
NO. 1 GUANIDINE TYPE-0.9%
NO. 2 " " 0.55%
NO. 9 ALDEHYDE AMINE TYPE-0.5%
INDEX NUMBERS
NO. 1 22.0
NO. 2 22.5
NO. 3 43
MIN. AT 99.5 °C.
12½
25
37½
50
TAKEN AT 66.5°C. OR 153°F.
INDEX NUMBERS
NO. 1 11
NO. 2 9.5
NO. 3 27
NO. 1 GUANIDINE TYPE-0.9%
NO. 2 " " 0.55%
NO. 9 ALDEHYDE AMINE TYPE-0.5%
HEIGHT OF BISCUITING, COUPEN IN MILLIMETRES
HRS. AT 66.5°C.
7½
15
22½
30
TIME
FIGURE 2


4000 LBS/SQ IN.
281 KGS/SQ CM.
3000
211
2000
141
1000
70
CURED AT 153°C. OR 307°F. 4.22 KGS/SQ CM. 60 LBS/SQ IN.
TYPE-TENSILE CURVES ON ACCELERATORS OF ALDEHYDE AMINE TYPE WHICH CURE AS FAST AS THE GUANIDINE TYPE.
NO. 3 ALDEHYDE AMINE TYPE
NO. 9 " " "
NO. 10 " " "
NO. 11 " " "
MIN. AT 153°C.
2½
5
7½
10
CURED AT 141°C. OR 287°F. 281 KGS/SQ CM. 40 LBS/SQ IN.
NO. 3 ALDEHYDE AMINE TYPE - 0.50%
NO. 9 " " " 0.50%
NO. 10 " " " 0.60%
NO. 11 " " " 1.00%
MIN. AT 141°C.
7½
15
22½
30
TENSILE STRENGTH
TIME
FIGURE 3

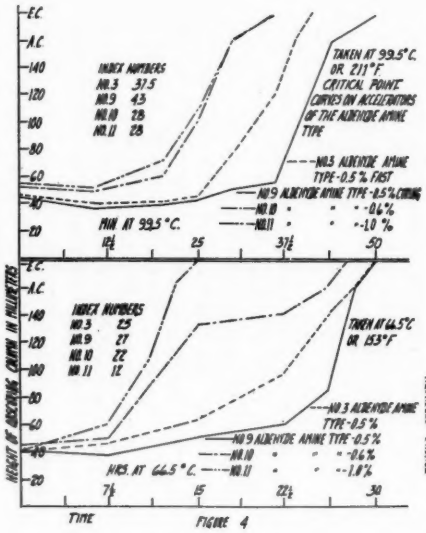


FIGURE 4

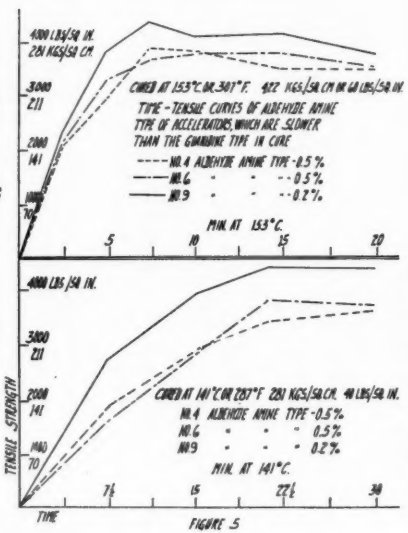

4200 LBS/SQ IN.
CURED AT 153°C OR 307°F. 422 KGS/SQ CM OR 60 LBS/SQ IN.
TYPE - TENSILE CURVES OF ALDEHYDE AMINE TYPE OF ACCELERATORS, WHICH ARE SLOWER THAN THE GUANIDINE TYPE IN CURE
NO.4 ALDEHYDE AMINE TYPE -0.5%
NO.6 " " -0.5%
NO.9 " " -0.2%
MIN. AT 153°C.
4000 LBS/SQ IN.
CURED AT 141°C OR 287°F 281 KGS/SQ CM. 40 LBS/SQ IN.
NO.4 ALDEHYDE AMINE TYPE -0.5%
NO.6 " " 0.5%
NO.9 " " 0.2%
MIN. AT 141°C.
TENSILE STRENGTH
TIME

FIGURE 5

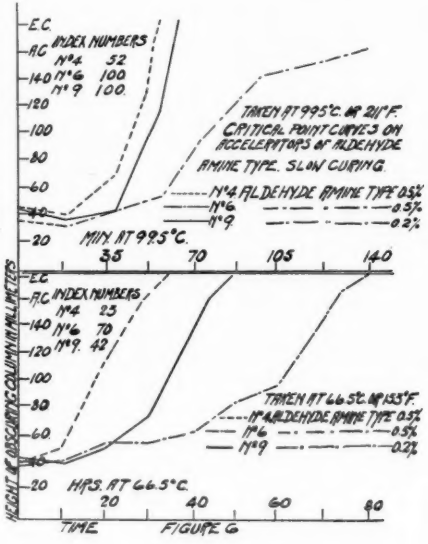


FIGURE 6

critical point, that actual values be obtained in order to designate the scorching tendencies clearly when comparing various accelerators, and also to render time-set up curves possible.

The method described herein is therefore based on the well-known facts of the so-called solubility of unvulcanized, and the insolubility of vulcanized, rubber in rubber solvents. The actual determination of solubility of the stock is made by measuring a dispersion of the pigment contained in the stock itself.

Inasmuch as zinc oxide in rubber is well dispersed when the raw rubber is dissolved in a solvent, it was decided to test the materials in the following formula:

Smoked sheets	100
Zinc oxide	95
Sulfur	3 to 4
Accelerator	Variable

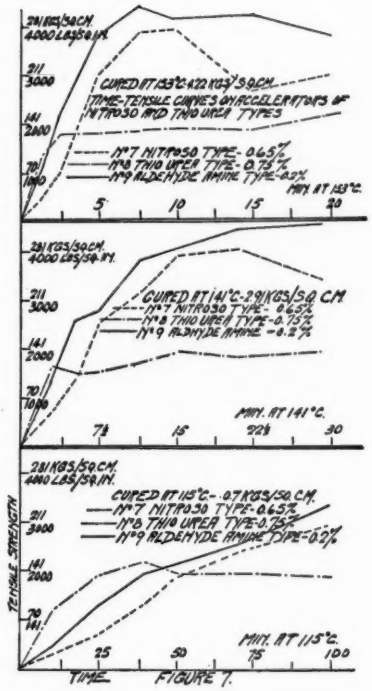
The sulfur was varied according to the accelerator used, and the accelerator content was made to obtain balanced standard cures.

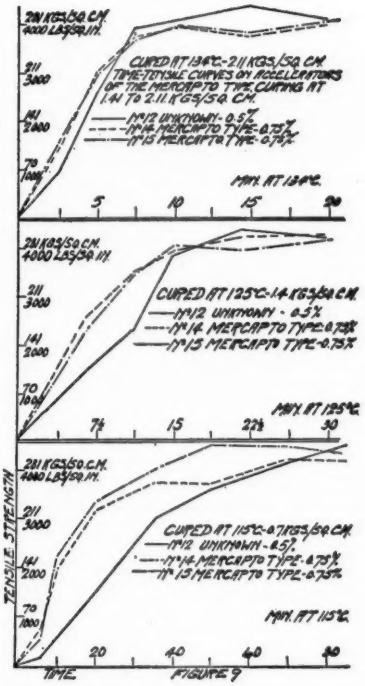
Samples were prepared from a sheet of uncured stock, containing the accelerators to be studied, which had been milled as nearly as possible under standard conditions. These samples were $^1/_8$ inch (3 mm.) thick, with holland on both sides, and were made by dieing out disks 0.5 inch (13 mm.) in diameter. These disks were then introduced into stoppered test tubes 15 mm. in diameter and 150 mm. high. Checks were made in each case and the samples were heated for a definite period, depending upon the material being tested. The samples were removed at intervals sufficient to give the progress of the vulcanization process.

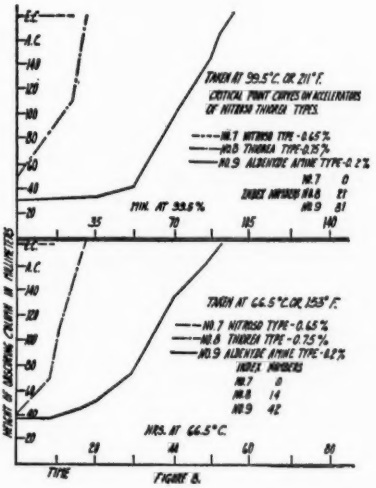
The samples were exposed to uniform heat in the vapor of constant-boiling liquid for a given time. A special bath was designed for this purpose. It contained 64 jackets, just large enough to hold the test tubes, soldered into the top and flush with it, extending inside the bath. A neck in the side of the bath permitted connection with a reflux condenser. The whole was made of copper and gave very accurate and even temperatures.

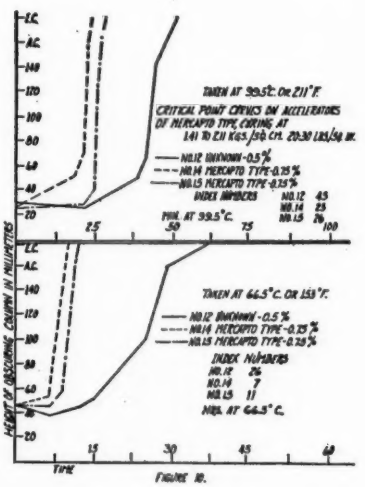
Two temperatures were selected for set-up determinations. The first was 99.5° ± 0.2° C., and was chosen because it was believed to be representative of the temperature to which an accelerator would be exposed in actual mill room practice. This was conveniently obtained by using water as the liquid in the bath. The other temperature was 66.5 ± 0.2° C., and was obtained by means of boiling methanol. This temperature represents approximately the temperature of stocks for 12 to 24 hours after calendering and rolling in liners for storage, and is purposely somewhat high. It is also approximately the temperature at which a number of ultra-accelerators are tested for air curing properties.

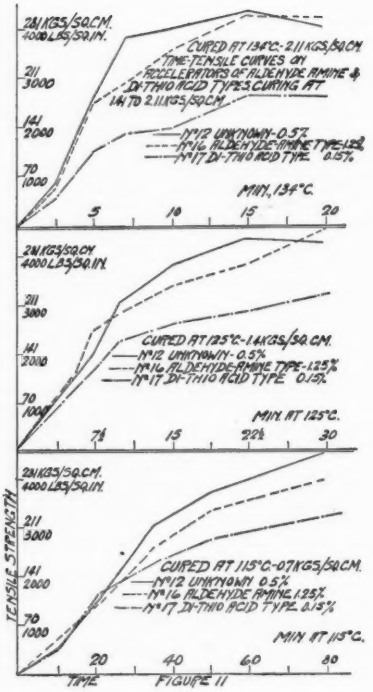
The solubility of the rubber sample, after it had been exposed to heat as described above, was determined by intro-

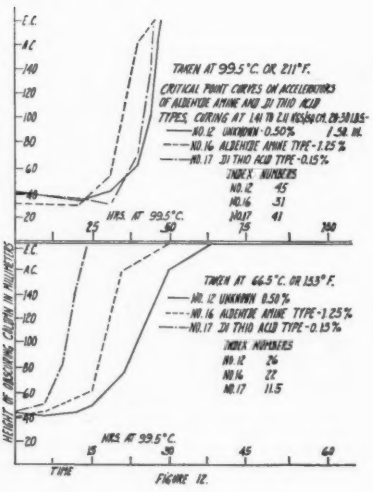

CURED AT 139°C-422 KGS/SQ.CM.
TIME-TENSILE CURVES ON ACCELERATORS OF NITROSO AND THIO UREA TYPES
N°7 NITROSO TYPE- 0.65%
N°8 THIO UREA TYPE- 0.75%
N°9 ALDEHYDE AMINE TYPE- 0.2%
MAX. AT 139°C.
CURED AT 141°C-2.9 KGS/SQ.CM
N°7 NITROSO TYPE- 0.65%
N°8 THIO UREA TYPE-0.75%
N°9 ALDEHYDE AMINE -0.2%
MAX. AT 141°C.
CURED AT 115°C- 0.7 KGS/SQ.CM.
N°7 NITROSO TYPE- 0.65%
N°8 THIO UREA TYPE-0.75%
N°9 ALDEHYDE AMINE TYPE-0.2%
MAX. AT 115°C.
TENSILE STRENGTH
TIME
FIGURE 7.


CURED AT 134°C-2.11 KGS/SQ.CM.
TIME-TENSILE CURVES ON ACCELERATORS OF THE MERCAPTO TYPE CURING AT 1.41 TO 2.11 KGS/SQ.CM.
N°12 UNKNOWN- 0.5%
N°14 MERCAPTO TYPE- 0.75%
N°15 MERCAPTO TYPE- 0.75%
MAX. AT 134°C.
CURED AT 125°C-1.4 KGS/SQ.CM.
N°12 UNKNOWN - 0.5%
N°14 MERCAPTO TYPE-0.75%
N°15 MERCAPTO TYPE-0.75%
MAX. AT 125°C.
CURED AT 115°C-0.7 KGS/SQ.CM.
N°12 UNKNOWN - 0.5%
N°14 MERCAPTO TYPE- 0.75%
N°15 MERCAPTO TYPE- 0.75%
MAX. AT 115°C.
TENSILE STRENGTH
TIME
FIGURE 9


TAKEN AT 99.5°C. OR 211°F.
CRITICAL POINT CURVES ON ACCELERATORS OF NITROSO THIOUREA TYPES.
N°7 NITROSO TYPE - 0.65%
N°8 THIOUREA TYPE-0.75%
N°9 ALDEHYDE AMINE TYPE-0.2%
INDEX NUMBERS
N°7 0
N°8 21
N°9 81
MIN. AT 99.5°C.
TAKEN AT 66.5°C. OR 153°F.
N°7 NITROSO TYPE - 0.65%
N°8 THIOUREA TYPE - 0.75%
N°9 ALDEHYDE AMINE TYPE - 0.2%
INDEX NUMBERS
N°7 0
N°8 14
N°9 42
MIN. AT 66.5°C.
HEIGHT OF CRACKING CHURN IN MILLIMETRES
TIME
FIGURE 8.


TAKEN AT 99.5°C. OR 211°F.
CRITICAL POINT CURVES ON ACCELERATORS OF MERCAPTO TYPE CURING AT 1.41 TO 2.11 KGS/SQ.CM. 20.30 LBS/SQ.IN.
N°12 UNKNOWN-0.5%
N°14 MERCAPTO TYPE-0.75%
N°15 MERCAPTO TYPE-0.75%
INDEX NUMBERS
N°12 43
N°14 25
N°15 76
MIN. AT 99.5°C.
TAKEN AT 66.5°C. OR 153°F.
N°12 UNKNOWN - 0.5%
N°14 MERCAPTO TYPE - 0.75%
N°15 MERCAPTO TYPE - 0.75%
INDEX NUMBERS
N°12 24
N°14 7
N°15 11
MIN. AT 66.5°C.
HEIGHT OF CRACKING CHURN IN MILLIMETRES
TIME
FIGURE 10.


CURED AT 134°C: 2.11 KGS/SQ.CM.
TIME-TENSILE CURVES ON ACCELERATORS OF ALDEHYDE AMINE & DI-THIO ACID TYPES CURING AT 1.41 TO 2.11 KGS/SQ.CM.
M*12 UNKNOWN-0.5%
M*16 ALDEHYDE-AMINE TYPE-1.25%
M*17 DI-THIO ACID TYPE 0.15%
MIN. 134°C.
CURED AT 125°C-1.41 KGS/SQ.CM.
M*12 UNKNOWN-0.5%
M*16 ALDEHYDE-AMINE TYPE-1.25%
M*17 DI-THIO ACID TYPE 0.15%
MIN. AT 125°C.
CURED AT 115°C-0.7 KGS/SQ.CM.
M*12 UNKNOWN 0.5%
M*16 ALDEHYDE AMINE 1.25%
M*17 DI-THIO ACID TYPE 0.13%
MIN. AT 115°C.
TENSILE STRENGTH
TIME
FIGURE 11

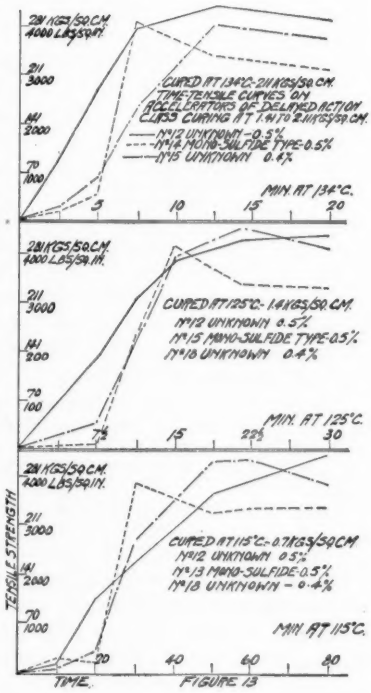

TAKEN AT 99.5°C. OR 211°F.
CRITICAL POINT CURVES ON ACCELERATORS OF ALDEHYDE AMINE AND DI THIO ACID TYPES, CURING AT 1.41 TO 2.11 KGS/SQ.CM. OR 20 TO 30 LBS-
NO.12 UNKNOWN-0.50% 1.50 WT.
NO.16 ALDEHYDE AMINE TYPE-1.25%
NO.17 DI THIO ACID TYPE-0.15%
INDEX NUMBERS
NO.12 45
NO.16 31
NO.17 41
HRS. AT 99.5°C.
TAKEN AT 66.5°C. OR 133°F.
NO.12 UNKNOWN 0.50%
NO.16 ALDEHYDE AMINE TYPE-1.25%
NO.17 DI THIO ACID TYPE-0.15%
INDEX NUMBERS
NO.12 24
NO.16 22
NO.17 11.5
HRS. AT 99.5°C.
HEIGHT OF ROCKING CURVE IN MILLIMETERS
TIME
FIGURE 12.

ducing the disk, from which the holland had been removed, into a 25 mm. test tube containing 50 cc. of 68–70° Bé. gasoline and then shaking the tube rapidly with a circular motion for exactly 1 minute, giving the sample 105 shakes during this period. The suspension of pigment was then poured off, only a small portion of the rubber being dissolved in this time, and readings were taken in an obscurometer, made after the description of Vogt,[6] with two simple modifications; red and green Duboscq color screens were put over the light source and the plunger in the auxiliary tube was eliminated. The shaking period of 1 minute was used as it was found that at this period a sample giving zero solubility had just the faintest trace of set-up when tested by stretching. It was also the point at which the edges of the stock started to wrinkle when immersed in the solvent instead of dissolving smoothly. This point, however, is not far enough along to render the rubber completely insoluble in gasoline, as it will give a dense suspension if left in the solvent 3 or 4 hours and then shaken, but is much before the time that time-tensile measurements can be relied upon to detect cure. Attention is called to the fact that the time of shaking can be varied in order to make the test more or less delicate, but the above procedure is the recommended one.

Vogt[6] and Lewis and Baker[7] show that the obscuring power of a suspension varies inversely as the concentration of the suspension when the same pigment is used. Therefore, the value, "height of obscuring column," used throughout this paper is an inverse measurement of the solubility of the rubber stock. Inasmuch as this relationship is simple, and rapidly obtained, calculations are not made to give concentrations, although this could be easily done, as follows:

X = grams per liter

$\frac{1000}{X}$ = concentration



[6] *India Rubber World*, **65**, 347 (1922).

[7] J. Ind. Eng. Chem., **12**, 890 (1920).

$$\text{O. P.} = \frac{\text{concentration}}{\text{height of column}}$$

O. P. for ZnO = 1000 sq. cm. per gram

Therefore $$1000 = \frac{1000/X}{\text{height of column}}$$

$$X = \frac{1000}{1000 \times \text{height of column}}$$

The "index number" is an arbitrary value taken as that increment of time at which the set up curve crosses the 140 mm. "height of obscuring column" ordinate. Practically, it is represented by a decided clearing up of the suspension. It is, of course, realized that in reading obscuring powers of suspensions of decreasing concentration the ultimate value is infinity. With the apparatus and volume of the suspension used, 150 mm. is the highest reading obtainable. This reading has a slight turbidity and any suspension which does not obscure the light, at 150 mm., or less, but still is turbid, is denoted as "almost clear."

Experimental

A list of accelerators used in the experimental demonstrations of the different phases encountered in this method of determining critical points is given below. These materials were used, not for the purpose of comparing the specific accelerators, but solely to illustrate this method of determining set up values. Some of the materials were supplied from the writer's laboratory and some are commercial products. For this reason the accelerators are listed only according to type, when this is known.

No.	Type	No.	Type
1	Guanidine	11	Aldehyde amine
2	Guanidine	12	Unknown
3	Aldehyde amine	13	Monosulfide
4	Aldehyde amine	14	Mercapto
6	Aldehyde amine	15	Mercapto
7	Nitroso	16	Aldehyde amine
8	Thiourea	17	Dithio acid
9	Aldehyde amine	18	Unknown
10	Aldehyde amine	20	Dithiocarbamate

Those accelerators of the same general behavior have been compared with each other and with a control stock. In general, there are four groups of accelerators in this list, classified on their behavior as follows:

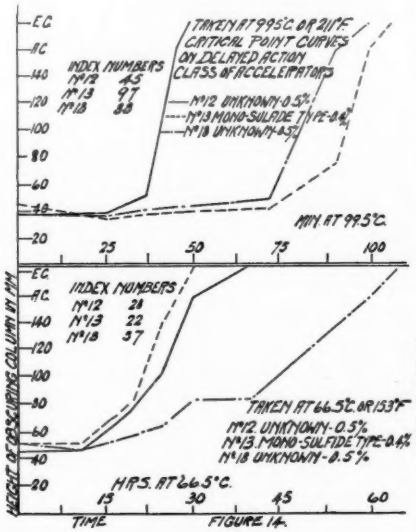
Group I—Fast curing accelerators to cure at 141° C. or 2.81 kg. per sq. cm. (287° F. or 40 lbs.) and above.

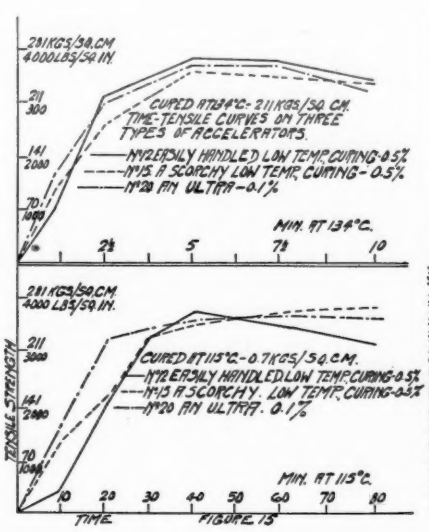
Group II—Accelerators to cure at 141° C. and above, which are distinctly slower than those included in the first group mentioned.

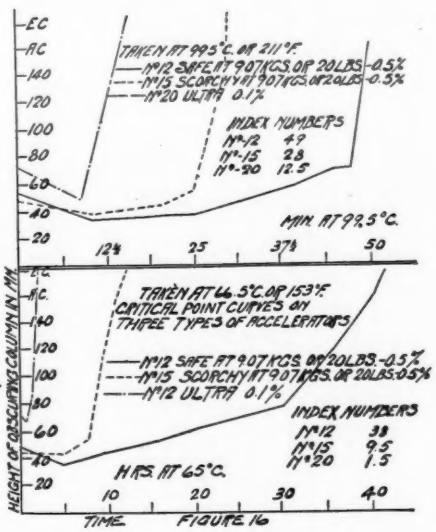
Group III—Accelerators curing 115° C. or 1.42 to 2.11 kg. (259° F. or 20 to 30 lbs.).

Group IV—One ultra-accelerator.

In presenting the results of the measurements of the critical points of these accelerators, the writer has chosen, for the sake of brevity, to show, first, the time-tensile curves in order to get an idea of the rate of cure of the stock studied and, second, the set up curves or the curves of the critical point determinations.


TAKEN AT 99.5°C. OR 211°F.
CRITICAL POINT CURVES ON DELAYED ACTION CLASS OF ACCELERATORS
INDEX NUMBERS
N°12 45
N°13 97
N°18 88
N°12 UNKNOWN-0.5%
N°13 MONO-SULFIDE TYPE-0.4%
N°18 UNKNOWN-0.5%
MIN. AT 99.5°C.
HEIGHT OF OSCILLATING COLUMN IN MM.
INDEX NUMBERS
N°12 28
N°13 22
N°18 37
TAKEN AT 66.5°C. OR 153°F
N°12 UNKNOWN-0.5%
N°13 MONO-SULFIDE TYPE-0.4%
N°18 UNKNOWN-0.5%
HRS. AT 66.5°C.
TIME
FIGURE 14.


211 KGS/SQ.CM.
4000 LBS/SQ IN.
CURED AT 134°C - 211 KGS/SQ. CM.
TIME-TENSILE CURVES ON THREE TYPES OF ACCELERATORS.
N°12 EASILY HANDLED LOW TEMP. CURING-0.5%
N°15 A SCORCHY LOW TEMP. CURING - 0.5%
N°20 AN ULTRA - 0.1%
MIN. AT 134°C.
211 KGS/SQ.CM.
4000 LBS/SQ IN.
CURED AT 115°C - 0.7 KGS/SQ.C.M.
N°12 EASILY HANDLED LOW TEMP. CURING-0.5%
N°13 A SCORCHY. LOW TEMP. CURING-0.5%
N°20 AN ULTRA. 0.1%
MIN. AT 115°C.
TENSILE STRENGTH
TIME
FIGURE 15


TAKEN AT 99.5°C. OR 211°F.
N°12 SAFE AT 9.07 KGS. OR 20 LBS - 0.5%
N°15 SCORCHY AT 9.07 KGS. OR 20 LBS - 0.5%
N°20 ULTRA 0.1%
INDEX NUMBERS
N°12 42
N°15 28
N°20 12.5
MIN. AT 99.5°C.
TAKEN AT 66.5°C. OR 153°F.
CRITICAL POINT CURVES ON THREE TYPES OF ACCELERATORS
N°12 SAFE AT 9.07 KGS. OR 20 LBS - 0.5%
N°15 SCORCHY AT 9.07 KGS. OR 20 LBS - 0.5%
N°12 ULTRA 0.1%
INDEX NUMBERS
N°12 38
N°15 9.5
N°20 1.5
HRS. AT 65°C.
HEIGHT OF OSCILLATING COLUMN IN MM.
TIME
FIGURE 16

In some cases special attention is given to the undercured portion of the time-tensile curves. Index numbers are given. All materials curing at 141° C. or above used 4 parts of sulfur per 100 of rubber in the base recipe. Those designed to cure at a lower temperature had 3 parts sulfur per 100 of rubber.

GROUP I—FAST CURING (40–60 LBS.) ACCELERATORS. *Figure 1.* The first class of accelerators studied is the guanidine type, which cures quickly at 141° to 153° C. (2.81 to 4.22 kg. per sq. cm. or 40–60 lbs.). These results show No. 1 and No. 2 to be very close together in rate of cure and slightly less rapid than material No. 9, which is serving as the control in this group.

Figure 2. The critical point curves taken at 99.5° C. show No. 1 and No. 2 set up in about the same period of time at this temperature, while No. 9 is much slower. The same is true of determinations made at 66.5° C.

Figure 3. The second class of accelerators in this group designed to cure at 2.81 kg. per sq. cm., or above, is practically as rapid as the guanidine type and contains the aldehyde-amine type materials.

The time-tensile curves show that the stocks are well balanced at 153° C. (4.22 kg.), with a slight difference in maximum tensile values. No. 11 might be considered a bit slow. The same general statements apply to the 141° C. (2.81 kg.) cures, with perhaps the conclusion that No. 9 is somewhat the fastest of the lot. If the undercured portions of the curves at both 2.81 and 4.22 kg. are considered, one would conclude No. 3 and No. 9 set up the fastest and about alike, followed by No. 10, and then by No. 11.

Figure 4. By measuring set up values, it is seen that at 99.5° C. there is little difference in No. 10 and No. 11, which cure in a shorter time than does No. 3. No. 3 cures more rapidly than No. 9. At 66.5° C., the materials rank as follows: No. 11, No. 10, No. 3, No. 9.

GROUP II—SLOWER CURING (40–60 LBS.) ACCELERATORS. *Figure 5.* The first class of this group of the accelerators curing at higher temperature are also aldehyde-amine condensation products, but cure at a slower rate than the materials in Group I. The control stock, containing No. 9 accelerator, has had the amount of accelerator decreased from 0.5 per cent to 0.2 per cent, which gives a rate of cure close to that obtained with No. 4 and No. 6 when cured at 153° C. (4.22 kg.), but is slightly more rapid when cured at 141° C. (2.81 kg.). The stocks containing No. 4 and No. 6 are close together in rate of cure at both temperatures.

Figure 6. Critical point determinations show that these three materials are widely different in their set up values, and that this is confirmed by the fact that, whereas the stock containing No. 9 accelerator burns in 40 minutes on a mill with a stock temperature of about 95° to 100° C., that containing No. 6 required 84 minutes.

Figure 7. The second class of this group of materials offers a very interesting contrast, in that one example demonstrates that the method of judging set up values by the position of the undercured portions of the time-tensile curves is satisfactory, while the other shows very clearly that this method is faulty.

The materials are the thiourea type compared with the nitroso type. The quantities were 0.75 per cent of the former and 0.65 per cent of the latter. The nitroso type stock is almost equal to the control in rate of cure, but the thiourea type stock is hopelessly slow. The stock was not further accelerated, however, in view of the results obtained.

At the 0.7-kg. (10-lb.) cure it is seen that the thiourea stock is much above the control on the undercured branch of the curve, which is not the case with the nitroso type stock. Considering

all cures, one would conclude by the time-tensile curve method of judging set-up that the thiourea type stock would perhaps set up faster than the control (No. 9), while the nitroso type stock would not.

Figure 8. The behavior actually experienced is shown by the critical point curves. Incidentally, the nitroso type stock burned on the mill at 95–100° C. in 6 minutes, the thiourea stock in 18 minutes, and No. 9 in 40 minutes.

The index number reading 0–0 means that, in spite of the fact that the time-tensile curves of the nitroso type materials are below those of the control, the nitroso stock was actually set up when control readings were made.

GROUP III—ACCELERATORS CURING AT 115° TO 134° C. *Figure 9.* The first class offers comparisons between three materials, two of which are reputed to require special care in handling. The time-tensile curves show that the rate of cure of the materials is practically the same at 134° C. (2.11 kg.) and 125° C. (1.4 kg.), while at 115° C. (0.7 kg.), No. 12 is decidedly slow.

Figure 10. Critical point determinations at the two temperatures show that No. 14 is slightly more scorchy than No. 15, and both are decidedly worse for burning than No. 12.

These materials burned on a 95–100° C. mill as follows:

No.	TYPE	MINUTES
14	Mercapto	7½
15	Mercapto	8½
12	Unknown	14½

Figure 11. The second class of this group is composed of one accelerator of the aldehyde-amine type and one of the dithio acid type. These stocks were designed so that the undercured portion of the time-tensile curve at 115° C. (0.7 kg. steam) would be the same as the control, regardless of the rate of cure in the higher portions of the curve. This resulted in the aldehyde-amine type stock approaching the control, while the dithio acid type is decidedly slow.

Figure 12. Critical point determinations show that at 99.5° C. these materials behave very similarly, but at 66.5° C. there is a decided tendency on the part of No. 17 to set up before the other two. This undoubtedly means that in warm storage this stock would set up before the others.

Figure 13. The third class of this group consists of two materials classified as "delayed action" accelerators. These two accelerators are compared with No. 12, which does not show this tendency. The time-tensile curves clearly demonstrate the delayed action tendencies of the two materials, at all the temperatures employed.

Figure 14. The critical point curves show Nos. 13 and 18 to be much slower in set-up at 99.5° C. than No. 12. Burning times were in the proportion of 1 to 5 when the stocks were milled on a hot mill. However, an unexpected behavior was exhibited at 66.5° C. in that No. 13 at this temperature sets up just as fast as does No. 12 and much faster than No. 18. If No. 18 were used as a standard of comparison, this might mean that it is possible for a stock containing No. 13 to be better than No. 18 as regards scorching on the mill, but that if the stock was piled, or rolled into liners while warm, No. 13 stock would, no doubt, set up more rapidly than the stock containing No. 18.

Figure 15. As a last example a series of stocks was selected containing accelerators of three different kinds as regards their action and use—namely, an ultra, a "touchy" 1.42–2.11-kg. curing accelerator, and an easily handled 1.42–2.11-kg. accelerator. These stocks were made to cure at approximately the same rate when cured at 134° C. (2.11 kg.) and the curves are reasonably close together. Cures at 115° C. (0.7 kg.) were made and show fair balance between the ultra and twenty-pound curing materials.

Figure 16. Critical point determinations on these stocks show that the materials arrange themselves according to their behavior, as known from experience, and this behavior is illustrated very aptly in their index numbers.

Conclusions

The determination of critical point curves for accelerators is of value in ascertaining their scorching tendencies. Also, the index number, defined as that increment of time at which the set-up crosses the 140 mm. "height of column" ordinate, is of value in comparing the scorching qualities of various accelerators. For accurate work the cures on the accelerators compared should be balanced at the temperature of use, and control obscuration readings should be fairly close together in their value. Stocks should be milled in as nearly the same manner as possible.

For the complete history of an accelerator's behavior, critical point determinations should be made at at least two and perhaps three, temperatures, one corresponding to the milling temperature, another to the warm storing temperature of stock after it has left the mill or calender, and a third to room temperature, although the experimental results on the last named are not complete at this time. If these determinations are made, the scorching tendencies of an accelerator under actual factory use can be predicted with accuracy.

Acknowledgment

The writer wishes to acknowledge the helpful criticisms of M. M. Harrison and H. A. Morton.

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Effect of Repeated Reclaiming of Rubber[1]

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The question is often asked—can rubber be repeatedly reclaimed without seriously affecting the quality of the reclaim? To throw some light on this point a sample of whole tire reclaim was cured, then regenerated in a laboratory devulcanizer, and the cycle repeated three times.

While repeated reclaiming had no effect on the tensile of the resulting reclaim, the modulus increased and elongation decreased with each successive cycle. The chloroform extract and plasticity decreased with an accompanying increase in combined sulfur.

The successive reclaims, incorporated in a low-quality tread compound, imparted progressively decreasing elongation and tensile, with increasing modulus. Contrary to expectation, there was but little evidence of increasing deterioration of aging properties, as far as could be judged by artificial aging.

WITH the increasing consumption of reclaimed rubber during the past decade, it is obvious that worn-out rubber articles now being returned for reclaiming are fairly high in rubber that has been once reclaimed. The extent to which the cycle of curing and reclaiming can be continued without serious deterioration in the properties of the reclaim merits the consideration of all those interested in the rubber reclaiming industry.

[1] Presented before the Division of Rubber Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

To the best of the writer's knowledge, the literature contains no reference or opinions on the subject which are confirmed by experimental data. Bishop[2] asserts that the question—how often can rubber be reclaimed before it is useless? —is foremost in the minds of rubber reclaimers. He fails to answer the question, simply recommending a segregation and separate processing of low quality scrap tires containing high percentages of reclaimed rubber. Winkelmann[3] dwells on the point, briefly stating:

> We sometimes hear the question as to what kind of reclaimed rubber will be obtained from vulcanized rubber which already contains substantial proportions of reclaim. If vulcanized rubber is disaggregated under proper conditions it may be possible to aggregate it on revulcanization so as to lose but little of original value.

In order to obtain the fundamental facts on which a conclusive answer might be based, the following experiments were performed in the laboratory. The natural cycle of curing and reclaiming of the rubber was simulated as closely as possible.

Experimental Procedure

A sample of whole tire reclaim (specific gravity 1.20) was selected for this experiment. A complete analysis of this reclaim is given in Table I.

Table I—Analysis of Whole Tire Reclaim

	Cor. Acetone Extract	$CHCl_3$ Extract	Ash	ZnO	Total Sulfur	Free Sulfur	Combined Sulfur[a]	Carbon Black
	%	%	%	%	%	%	%	%
Original	10.5	22.0	20.5	10.0	2.82	0.07	2.75	6.00
Cycle IV	21.7	5.2	21.2	8.4	8.56	0.51	8.05	6.32

[a] By difference.

This reclaim was then mixed on a 12 × 6 inch (30 × 15 cm.) laboratory mill using formula I.

	Formula I	Formula II
Reclaim	100.00	84.00
Smoked sheets	....	50.00
Sulfur	1.90	2.75
Gas black	....	45.00
Zinc oxide	....	5.00
Pine tar	....	5.00
Di-*o*-tolylguanidine	0.30	0.50
	102.20	192.25
Total rubber	60.00	100.00
Sulfur to rubber	2.75 per cent	2.75 per cent
Accelerator to rubber	0.50 per cent	0.50 per cent

This formula was chosen because it supplied the amount of sulfur and accelerator that would be available to the reclaim in the average practical compound. The reclaim mixture was then cured in a 24-inch (61-cm.) steam heated platen press using 450 pounds (31.7 kg.) hydraulic pressure. A 25 minute cure at 141.1° C. was selected because this cure

[2] *Rubber Age (N. Y.)*, **21**, 189 (1927).
[3] Ind. Eng. Chem., **18**, 1163 (1926).

gave maximum tensile in the reclaim. About 3600 grams of this material were cured in 0.25 cm. (0.10 inch) slabs, which were cut into pieces approximately 1 sq. cm. to be used as scrap for reclaiming. Stress-strain data on 15- and 25-minute cures of this original reclaim were obtained, breaking four dumbbell strips per cure. All figures were corrected to a testing temperature of 27.7° C., basing the figures on the temperature correction curve used by Palmer.[4]

A sample of the original reclaim was also incorporated in the low quality tread mixture shown under formula II. A tread containing such a high concentration of reclaim was chosen in order to exaggerate any differences in the successive reclaims. The sulfur and accelerator relations were the same as in formula I.

A series of cures on this tread ranging from 40 to 100 minutes in 10 minute intervals was obtained, curing in a paraffin bath at 143.3° C. Tests were made on two strips

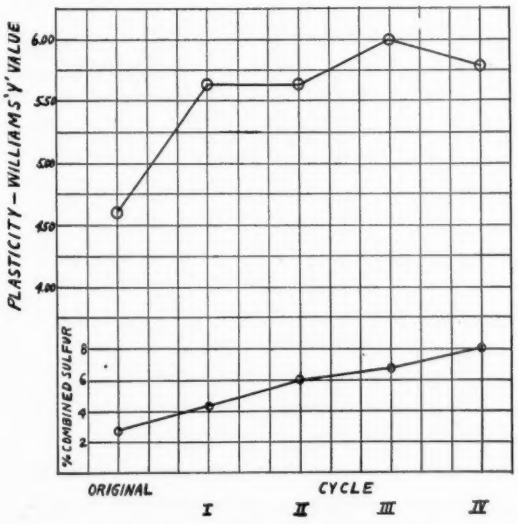

Figure 1—Plasticity *vs.* Combined Sulfur of Reclaim

per cure, stress at 400 per cent elongation and elongation and tensile at break being obtained. Test data are plotted in Figures 4, 5, and 6. After a study of the test figures, the 50-minute cure was selected as the best commercial cure of this tread. Such cures were then made in the press and dumbbell strips cut from the cured slabs were aged in an oven kept at 70° C.

The scrap obtained from the cured slabs of the original reclaim was then devulcanized for 9 hours at 184.4° C. (12.3 kg. per sq. cm. gage pressure) using the laboratory devulcanizer described by Shepard, Palmer, and Miller.[5]

[4] IND. ENG. CHEM., **19**, 1030 (1927).
[5] *Ibid.*, **20**, 143 (1928).

Enough 10 per cent sodium hydroxide solution to cover the scrap entirely was used. In the first run 3 per cent of pine tar, based on the weight of the scrap, was added in the devulcanizer. In the later runs the same amount was added but only 2 per cent was added in the devulcanizer and the remainder on the massing mill. This change made the processing of the reclaim more satisfactory. At the end of the cook the devulcanizer was removed from the furnace and allowed to cool overnight. The charge was then dumped on a wire screen, washed with tap water, and dried for 24 hours at a temperature varying from 50° to 70° C.

The reclaimed scrap was then massed on a laboratory mill having a refiner knife on the back roll. As soon as

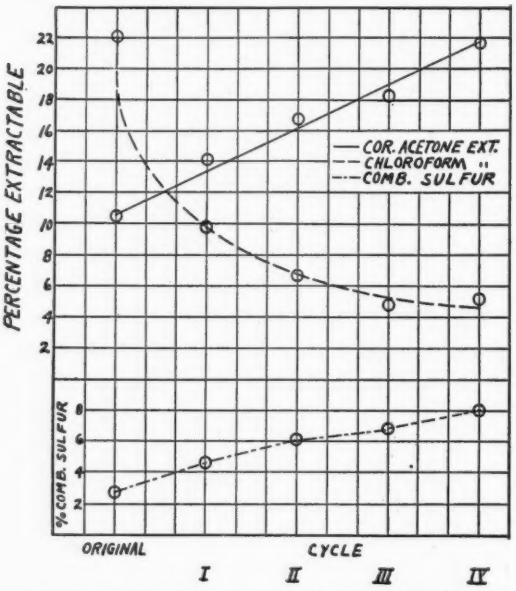

Figure 2—Extract *vs.* Combined Sulfur of Reclaim

the scrap knit together and covered the roll, the rolls were tightened until the reclaim rolled off in a sheet approximately 0.02 cm. (0.008 inch) in thickness. After six passes through the refiner the reclaim was rolled up and cut off in the form of a slab. A sample of this reclaim was saved for analysis, physical tests, and incorporation in the tread compound, and the remainder cured up for scrap for the next batch of reclaim.

Each sample of reclaim was analyzed for acetone extract and free and total sulfur, according to the recommendations of the Bureau of Standards Bulletin 38. The chloroform extract on the uncured reclaim was run 72 hours. Plasticities of the reclaim were run at 100° C. by the method of

Williams.[6] A 5-minute *Y* value was obtained on buttons punched from the refined slab of reclaim. This did not give true plasticity, but showed the trend of change of softness.

This cycle of curing and reclaiming was repeated three times, thus putting the original reclaim through four complete cycles of curing and subsequent devulcanization.

Effect on Uncured Properties of Reclaim

The figures in Table II illustrate the effect of repeated curing and reclaiming on both chemical and physical properties of the reclaim itself.

Figure 1 shows a progressive increase in combined sulfur with each cycle. The plasticity *Y* value curve shows an upward trend reflecting in a degree the decrease in plasticity

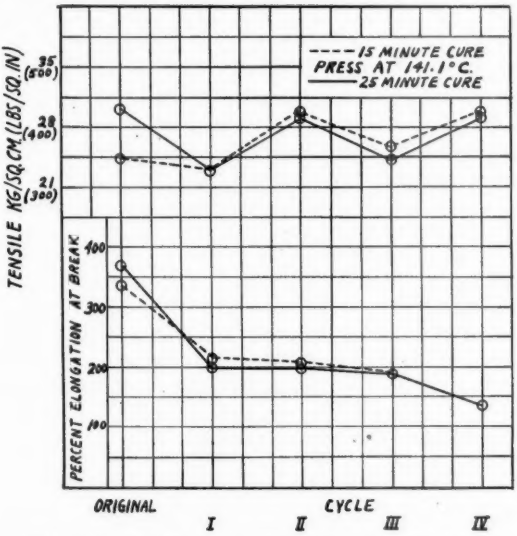

Figure 3—Tensile Strength of Successive Reclaims

with repeated reclaiming and gradually increasing chemical state of cure. The plasticity values in no way indicate the real change which took place in the reclaim. A hand examination of the successive samples of reclaim reveals a gradual change from the soft, pliable "feel" in the original reclaim to a stiff, leather-like condition in the final reclaim. The original reclaim, after refining, formed an almost homogeneous slab, while the reclaimed reclaims showed increasingly distinct lamination. The final product was so dry and stiff that it could not be "plied up" into a slab.

The effect of repeated reclaiming on the chloroform and acetone extracts as compared with the increase in combined sulfur is seen in Figure 2. The increase in acetone extract can be almost entirely accounted for by the amount of sof-

[6] IND. ENG. CHEM., **16**, 362 (1924).

tener added in each cycle of reclaiming. The curve showing the decrease in chloroform extract is much more significant. The extract decreases with each successive cycle, all points occurring on a logarithmic curve. The results indicate that with increase in combined sulfur the rubber hydrocarbon becomes more and more resistant to the disaggregating effect of heat. This confirms the experiments of Boiry,[7] in which slabs of cured rubber were subjected to high temperatures. In this work pure gum mixtures containing 2 and 10 per cent of sulfur, respectively, were cured 20 hours at 143° C. and then subjected to a 5 hour period of heating at 200° C. The slab having 2 per cent sulfur gave an extract of 37.8 per cent, while the slab having 10 per cent sulfur, and naturally a higher chemical state of cure, yielded only 19.2 per cent in extract. For this reason Boiry recommends that the coefficient of vulcanization of rubber which is to be reclaimed should be as low as possible, if a high quality reclaim is desired.

The chloroform extract figures give a more complete picture of the changes in the plasticity of the reclaim than the *Y* values shown in Figure 1. The figures show a maximum decrease in extract of 77 per cent, and this is more nearly an indication of the change in the plasticity and workability of the reclaim. This relation between the extract and plasticity confirms the opinion of Winkelmann,[3] who writes: "The plasticity of reclaimed rubber is, no doubt, dependent on the chloroform extract."

A comparison of the analysis of the final reclaim with that of the original is shown in Table I. The ash content is practically the same, the zinc oxide showing a slight decrease, probably due to the formation of soluble zinc salts. The carbon black content remains unchanged.

Effect on Cured Properties of Reclaim

The effect of repeated reclaiming on the tensile and elongation of the cured reclaims is shown in Figure 3. There was little or no effect on the stress at break. After the first cycle there was a distinct drop in elongation at break. The decrease in elongation continued with each successive reclaiming, but was not so marked as the first drop. The modulus figures were not plotted, since the drop in elongation made it necessary to obtain the stresses at lower and lower elongation; hence they are quite erratic. The figures as tabulated in Table II show, however, that the reclaim stiffened with each cycle. This stiffening effect was not peculiar, considering that the combined sulfur rose from 2.75 to 8.05 per cent.

Effect on Properties of a Tread

The modulus, tensile, and elongation figures of the tread in which the successive reclaims were incorporated are shown in Figures 4, 5, and 6. Compared with the tread containing

[7] *Rev. gén. caoutchouc*, Spec. No. (Livre d'or), p. 250 (January, 1927).

Table II—Effect on Reclaim Itself

Reclaim	Plasticity 5 Min. at 100° C. *Y* Value	Acetone Extract %	$CHCl_3$ Extract %	Total Sulfur %	Free Sulfur %	Combined Sulfur[a] %	Press-Cured at 141.1° C. *Minutes*	Modulus at: 100% *Kg. per sq. cm.*	200%	300%	Tensile	Elongation at Break *Per cent*
Original	4.6	10.5	22.0	2.82	0.07	2.75	15	..	12	20	27	370
							25	..	15	25	31	335
I	5.6	14.2	9.8	4.62	0.23	4.39	15	..	22	..	24	195
							25	..	20	..	24	215
II	5.6	16.8	6.7	6.40	0.27	6.13	15	..	27	..	30	195
							25	..	30	..	31	205
III	6.1	18.3	4.8	7.59	0.77	6.82	15	12	..	..	25	185
							25	13	..	..	26	185
IV	5.8	21.7	5.2	8.56	0.51	8.05	15	23	..	..	30	135
							25	25	..	..	31	135

[a] By difference.

the original reclaim, the first cycle reclaim tread shows a drop in tensile and elongation for all cures. A considerable increase in modulus, which reflects a stiffening of the reclaim itself, is noted. The tread containing the second-cycle reclaim shows no increase in modulus over the previous tread,

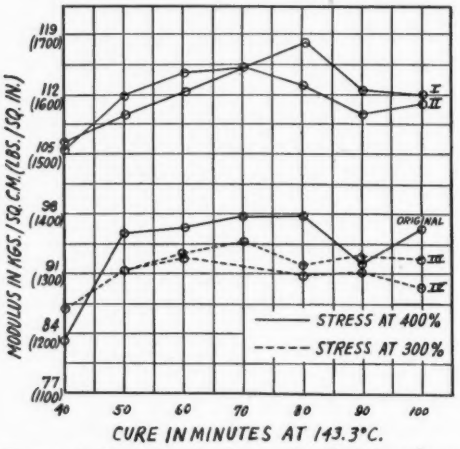

Figure 4—Modulus in Successive Reclaims in a Tread Mixture

but there is a decided drop in tensile. The decrease in tensile continues in the same order for the remaining third and fourth treads. After the first cycle an increase in the stiffness of the treads does not occur.

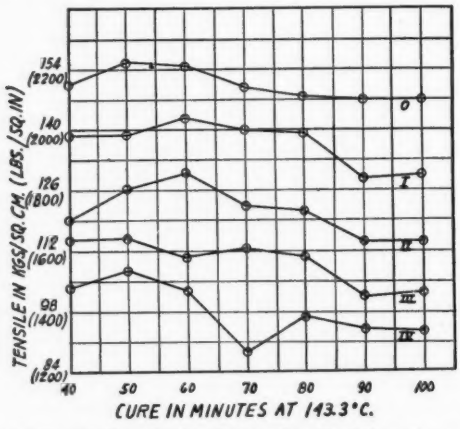

Figure 5—Tensile in Successive Reclaims in a Tread Mixture

The successive reclaims themselves had, within experimental error, the same tensile strength, but they did not produce identical tensile strength when cured in a tread. Evaluated in this practical way the deteriorating effect of

repeated reclaiming becomes more evident. Winkelmann[3] has shown that too much confidence should not be placed on the tensile of the cured reclaim. Working from another viewpoint, he experimented with reclaims which varied greatly in tensile strength, finding that high tensile in the reclaim was not always reflected in a high tensile in a mixture in which it was incorporated. For instance, a reclaim having 1200 to 1300 pounds (84.5 to 91.5 kg. per sq. cm.) tensile strength when mixed in friction stocks imparted no better tensile properties to the cured mixture than a reclaim having 250 to 350 pounds (17.5 to 24.6 kg. per sq. cm.) tensile. Commenting on this fact, he writes: "The physical properties of a reclaimed rubber in the uncured state are fully as important, and often more so, than physical tests on the cured reclaim."

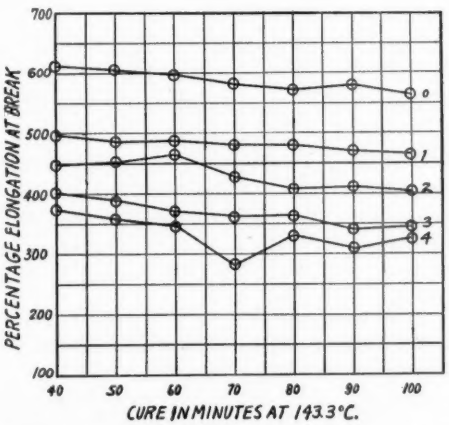

Figure 6—Elongation in Successive Reclaims in a Tread Mixture

The effect of continued reclaiming on the aging properties of the reclaim is best seen in Figure 7. Tensiles of the treads containing successive reclaims are plotted, showing the deterioration resulting from 7, 14, and 21 days of oven aging at 70° C. As judged by these figures, the first cycle tread deteriorated more rapidly than the one containing the original reclaim. The remaining treads, however, show no more serious rate of deterioration than the original reclaim tread. The artificially aged figures, taken as a whole, give little evidence that repeated reclaiming had a deteriorating effect on the aging properties of the reclaim. Shepard, Palmer, and Miller[5] have shown that a tread containing a low combined-sulfur reclaim aged better than one which contained a similar reclaim with higher combined sulfur; but they were working with reclaims which had considerably lower combined sulfur than even the original reclaim of this experiment. It is probable that with increasing combined sulfur in the re-

claim the deterioration when aging reaches a maximum which is not exceeded when the combined sulfur is further increased.

Discussion of Results

In interpreting these data in terms of commercial significance, the severe nature of the experimental procedure must be taken into consideration, as otherwise a pessimistic view of the situation as regards the reclaim of the future will be taken. It must be considered that these experiments greatly exaggerated the effects of repeated reclaiming, since the original reclaim was devulcanized over and over again without an addition of new rubber in the successive cures.

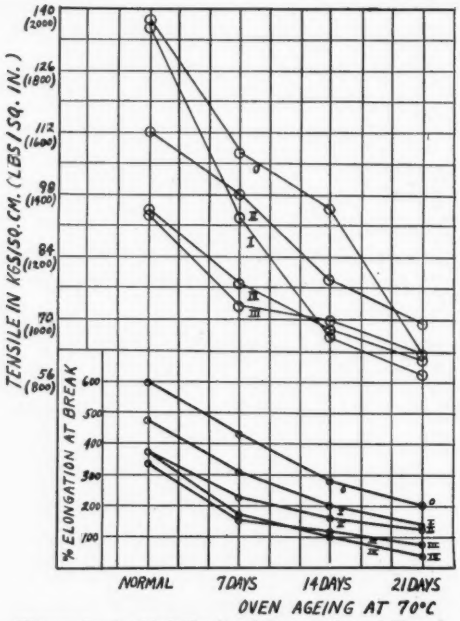

Figure 7—Artificially Aged Properties of Tread

The reclaimer is seldom, if ever, called upon to reclaim a scrap consisting of 100 per cent reclaim.

To emphasize the degree of exaggeration, take a whole-tire scrap, 40 per cent of the rubber content of which is once-reclaimed rubber, the remaining 60 per cent being once-cured but never-reclaimed rubber. If this scrap is devulcanized and 40 per cent of the resulting reclaim is put in a new tread, then 16 per cent of this reclaim is twice-reclaimed rubber and 24 per cent is once-reclaimed rubber. Continuing this through another cycle, a new 40 per cent reclaim tread would contain only 6.4 per cent of thrice-reclaimed rubber, 9.6 per cent of twice-reclaimed rubber, and 24 per cent of once-reclaimed rubber. So in practice, the amount of repeatedly-reclaimed rubber becomes, through dilution, a comparatively small part of the total reclaim.

As confirmatory evidence of the effect of dilution, a whole-tire scrap made from tires known to contain 25 to 40 per cent of reclaimed rubber on the formula, was devulcanized in the laboratory. Factory-blended whole tire scrap was reclaimed in a similar experiment as a control. The amount of softener added to the high reclaim scrap was reduced 50 per cent, because it was considered already high in softener content due to the reclaim. Tests on the resulting reclaims are shown in Table III.

Table III—Comparison of a Regularly Blended Scrap with a High Reclaim Scrap

(Devulcanized 9 hours at 184.4° C.)

Kind of Scrap	Softener	Plasticity P Value	Acetone Extract	Press Cure at 141.1° C.	Stress at Break	Elongation at Break
	%	*Hours*	%	*Minutes*	*Kg./sq. cm.*	%
Regularly blended	5	2.54	10.1	15	42	415
				25	45	250
25 to 40% reclaim	2.5	2.42	9.6	15	35	430
				25	49	445

As far as could be ascertained, the reclaims were comparable in workability as judged by plasticity figures and hand examination. The reduction of softener proved to be in the right direction, since the acetone extracts of the two reclaims are practically the same. The reclaim made from scrap which was already fairly high in reclaim had a tensile as good as and an elongation somewhat better than the control.

The above experiment made it evident that a fairly high concentration of reclaim in the scrap had but little effect on the quality of the reclaim and even this concentration exaggerated the conditions met in practice. Statistics compiled in this company's laboratories indicate that approximately 40 per cent of the scrap tires received by the reclaimer contain reclaimed rubber. Tires containing reclaimed rubber have been reclaimed for a number of years without any decrease in the quality of the reclaim. In fact, the quality of reclaimed rubber is improving from year to year, and it is probable that, in spite of the "reclaiming of reclaim," this upward trend in quality will continue as research leads to better methods of manufacture.

Conclusions

1—Reclaimed rubber, without the addition of new rubber in a subsequent vulcanization, cannot be repeatedly cured and reclaimed without a considerable deterioration in its physical properties.

2—The rubber scrap for reclaiming should be intelligently blended, and an endeavor made to keep the concentration of once-reclaimed rubber as low as is economically possible.

3—The chloroform extract and sulfur analyses of the uncured reclaimed rubber yield valuable information in regard to the quality of the product.

Acknowledgment

The writer wishes to express his appreciation to N. A. Shepard and H. F. Palmer for their many valuable suggestions relative to the experiments and the writing of this paper.

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Principles of Patent Law Involved in the Weiss Patent Litigation[1]

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OWING to the widespread interest in the chemical industry generally, and especially in the rubber industry, in diphenylguanidine as an accelerator in the vulcanization of rubber, it is believed that a discussion of the recent decision of the Supreme Court of the United States in the matter of the Weiss diphenylguanidine patent will serve a dual function of informing chemists about the status and the history of the Weiss patent and, at the same time, of expounding some of the principles of patent law involved in the case.

The Weiss patent No. 1,411,231 was litigated in the Federal Courts of the Second and Third Circuits of the United States before the Supreme Court took jurisdiction of the case. The Circuit Court of Appeals for the Second Circuit decided that the patent was invalid, in the case of Dovan Chemical Corporation *vs.* National Aniline and Chemical Company (292 Federal Reporter 555), whereas the Circuit Court of Appeals for the Third Circuit held that the patent was valid, in the case of Dovan Chemical Corporation *vs.* Corona Cord Tire Company (16 Federal Reporter, 2nd Series, 419). Whenever there is a diversity of holdings between different Circuit Courts of Appeals the Supreme Court will grant a Writ of Certiorari and take the case for final adjudication. As everyone probably knows, a decision of the Supreme Court of the United States is the supreme law of the land and is the

[1] Received June 21, 1928.

[2] Counsellor at Law and Patent Attorney.

final word on the matter in controversy throughout the jurisdiction of the United States.

Letters Patent, being a creature of the law and being dependent on the Patent Statutes and on a provision of the Constitution, must comply and conform with the various parts of the law in order to be valid. As the Patent Laws state, an inventor may, upon due proceedings had and upon payment of fees as required by law, obtain a patent. When the prerequisites of the statutes have not been satisfied, then the Letters Patent, although granted by the Patent Office, are not valid and are open to attack. In the present case the Weiss patent was issued, but it was vulnerable when subjected to the defenses available to an infringer.

Nature of Weiss Patent

The Weiss patent relates broadly to the vulcanization of rubber and more particularly to a vulcanization accelerator known as diphenylguanidine. The object of the invention was to improve the quality of vulcanized rubber goods and to reduce the time required for vulcanization. Weiss admitted in his patent that it was known that the addition of certain organic substances, such as triphenylguanidine, to a rubber mix caused the rubber to react more rapidly and thoroughly with sulfur due to a catalytic or similar action. The patentee stated, however, that he had discovered that a disubstituted guanidine, particularly diphenylguanidine, was especially useful as an accelerator of vulcanization and gave improved results. A specific example relative to the steps to be followed and the proportions of the various ingredients to be used was given. In the patent two types of claims were incorporated—one relating to a process of vulcanizing in the presence of a disubstituted guanidine or in the presence of diphenylguanidine, and the other relating to a product of rubber containing a disubstituted guanidine or diphenylguanidine. The claims which were in controversy were claims 4, 8, and 12 relating to the product and claims 1, 5, and 9 relating to the process.

Affidavit of Completion of Invention

While the Weiss patent application was pending in the Patent Office, it was rejected on an article entitled "The Action of Certain Organic Accelerators in the Vulcanization of Rubber," written by George Kratz and published in April, 1920, in the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY. The filing date of the Weiss application was November 12, 1921, which was about one year and seven months after the publication of the Kratz article. Since the publication was not more than two years prior to the filing date, an inventor can make an affidavit under Rule 75 of the Rules of Practice of the Patent Office, setting forth facts which show a completion of the invention in this country

before the date of the printed publication, and also stating that the inventor does not know and does not believe that the invention has been in public use or on sale in this country, or patented, or described in a printed publication in this or any foreign country for more than two years prior to his application, and that he has never abandoned the invention, so that the publication shall not constitute a bar to the grant of a patent. Weiss made an affidavit that D.P.G. (diphenylguanidine) was produced and actually used "in the vulcanization of rubber goods, such as hose, tires, valves, and other mechanical goods" during the early part of the year 1919. Daniels, a fellow chemist, who claimed to have been with Weiss at the time of the discovery in the laboratory of the Republic Rubber Company at Youngstown, made an affidavit of similar import. After these affidavits were filed, the Patent Office examiner allowed the Weiss application. The evidence brought out during the litigation showed, without contradiction, that the only rubber goods Weiss made during the early part of the year 1919 with D.P.G. were experimental test slabs of rubber in which D.P.G. was the accelerator, and that in fact neither Weiss nor anybody in the Republic Rubber Company had vulcanized commercial rubber goods such as hoses, tires, belts, valves, and other mechanical goods, before the Kratz publication. The petitioner, the Corona Cord Tire Company, contended that the Weiss patent was secured by false evidence and, therefore, was not entitled to the presumption of validity which ordinarily accompanies the grant of a patent. This contention was not sustained by the Supreme Court, which held, in effect, that since the test slabs were vulcanized with D.P.G. there was a completed and demonstrated discovery constituting a reduction to practice, and that the production of commercial rubber goods for use or for sale was not indispensable to the granting of a patent. The presumption of validity of the Weiss patent was consequently not destroyed.

This incident in the case shows how important it is for those who are doing research and experimental work to keep accurate, full, and complete records, which are properly dated and witnessed, so that no embarrassment need be experienced whenever it becomes necessary to prove the completion of an invention. It might be noted in passing, that it is well to have the witness affix the date in his own handwriting next to his signature in order to avoid any dispute regarding the date.

With respect to the question of the completion of invention, the Supreme Court laid down a complete and helpful ruling as to when an invention is reduced to practice. The doctrine is so important that the very language of the Supreme Court is quoted, to wit:

> A process is reduced to practice when it is successfully performed. A machine is reduced to practice when it is assembled, adjusted, and used. A manufacture is reduced to practice

when it is completely manufactured. A composition of matter is reduced to practice when it is completely composed.

A chemist who is concerned with patent law will have no trouble in deciding when an invention has been completed or reduced to practice if he will use the tests given by the Supreme Court.

Discovery of Catalysts Decreed Patentable

A further contention of the petitioner was that the claims of the Weiss patent, covering D.P.G. as a vulcanization accelerator, were invalid because the utility of D.P.G. as an accelerator was plainly indicated by general chemical knowledge and did not involve patentable discovery after triphenylguanidine had proved to be a good one for the vulcanization of rubber. In other words, one skilled in the art could have done what Weiss did by merely using knowledge which was fully and readily available to everybody in the art and without exercising any inventive faculty whatever. The Supreme Court disagreed with this contention by saying that "the catalytic action of an accelerator cannot be forecast by its chemical composition, for such action is not understood and is not known except by actual tests." Since the doctrine enunciated with respect to vulcanization accelerators is clearly applicable to every catalyst, a discovery that a material is useful as a catalyst should be patentable under the Supreme Court's holding. This should be very encouraging and very useful to chemists who are engaged in discovering new catalysts for various industrial processes throughout the chemical industry.

Contention of Prior Publication Untenable

Although the original Kratz paper as read before September 6, 1919, was set up as a defense against the Weiss patent, the Supreme Court held that, since it was not published until April, 1920, which was subsequent to Weiss's discovery and which was less than two years prior to the Weiss application, the original paper could not be used as a basis for a defense against the patent under Section 4886 of the Revised Statutes. It is only printed publications which have been published more than two years before the filing date of a patent that can be used as absolute defenses against a patent. Kratz read his original paper at the Philadelphia meeting of the AMERICAN CHEMICAL SOCIETY prior to September 6, 1919, which was more than two years before the filing of the Weiss application on November 12, 1921. The reading of a paper before a scientific or technical society or the like, therefore, is not a publication within the purview of Section 4886, and is not equivalent to publishing the paper as a printed publication.

Points upon Which Claims Were Invalidated

We now come to a consideration of the defense which was effective in causing the claims covering diphenylguanidine

as an accelerator for rubber vulcanization to be invalidated. The defense is that the invention had been in public use or on sale in this country more than two years prior to the filing of the patent application. It was proved that one George Kratz had used D.P.G. as an accelerator in the manufacture of three hundred tubes for automobile tires in August, 1917, at the Falls Rubber Company of Cuyahoga Falls, Ohio. These tubes were part of a special order of one thousand tubes which were sold to a purchaser, who gave his approval to the whole lot of tubes. Since this use and sale of D.P.G. as an accelerator was more than two years before the filing date of the Weiss patent, the Supreme Court held the defense to be good and the claims in suit, directed to D.P.G. as an accelerator for vulcanization of rubber, to be invalid. Anybody is now free to utilize the subject matter of the invalidated claims. It is to be observed in passing that if one public use of the invention or one sale of an embodiment of the invention can be proved to have occurred more than two years before the filing date of the patent, claims in the patent covering the invention in question will be declared to be invalid.

Weiss, in addition to claiming D.P.G. as a vulcanization accelerator, claimed a process of treating rubber by combining with the rubber compound "a disubstituted guanidine." It was shown that the class of disubstituted guanidines contains between fifty and one hundred substances in addition to D.P.G. The experts testified that many of these substances are not accelerators at all. Weiss made no disclosure in his patent that there is a general quality common to disubstituted guanidines which made them all effective as accelerators, and, therefore, could not make claims covering a broad class of substances many of which are not effective or useful as vulcanization accelerators. A patentee can only make claims which are directed to his invention and which include things that are effective for carrying the invention into practice. The doctrine enunciated by the Supreme Court in the Incandescent Lamp Patent Case (159 U. S. 465) prohibits the sustaining of claims which are not supported by a description in the specification showing that there is some quality running through the members of the family or class of substances which the patentee seeks to monopolize. In view of the Supreme Court's holding, the public is free to utilize the subject matter of the invalidated process claims.

The Weiss process claims in suit were also invalid because they were anticipated by an article published by one Du Bosc on July 15, 1919. This publication constituted a valid anticipation because it was printed more than two years before the filing date of the Weiss patent, which was November 12, 1921. For a full appreciation of the defense of prior publication as well as other defenses, reference should be had to Section 4920 of the Revised Statutes, which enumerates the defenses available to an infringer in actions for infringe-

ment. This section states, in essence, that when a person is charged with infringing a patent he may plead as a defense that:

1—The description and specification filed by the patentee was made to contain less than the whole truth relative to his invention or discovery, or more than is necessary to produce the desired effect.

2—The patentee had surreptitiously and unjustly obtained the patent for that which was in fact invented by another who was using diligence in adapting and perfecting the same.

3—The invention was patented or described in some printed publication prior to the patentee's supposed invention or discovery thereof, or more than two years prior to the application for a patent therefor.

4—The patentee was not the original and first inventor or discoverer of any material and substantial part of the thing patented.

5—The invention had been in public use or on sale in this country for more than two years before the application for a patent, or had been abandoned to the public.

From a perusal of the foregoing, it will be observed that, in view of the evidence, the Supreme Court was correct in its decision because (1) Kratz and not Weiss was proved to be the original and first inventor or discoverer of D.P.G. as a vulcanization accelerator; (2) D.P.G. was used as an accelerator and was sold in inner tubes for automobile tires more than two years before the filing of the Weiss patent application; and (3) Du Bosc described in a printed publication more than two years prior to the supposed Weiss invention or discovery that disubstituted guanidines had been used as accelerators.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 4, No. 1, pages 68–81 (1928).]

Organic Rubber Colors

W. J. S. Naunton

DYESTUFFS are divided into about twelve main groups according to their method of manufacture; thus we have the sulfur colors, which are made by fusing together various organic compounds with sulfur and sodium sulfide, the azo colors in which the intermediates are coupled together by means of the diazo reaction, and so on.

Most of the organic dyestuffs may be regarded as salts in which either the colored organic base is combined with a colorless inorganic acid (basic dyes) or the colored organic acid is combined with a colorless inorganic base (acid dyes). This salt formation has in most cases rendered the color soluble in water. In the absence of salt-forming groups in the colored compounds, or when their action is insufficiently potent, the resulting substances are sufficiently insoluble in water to be of direct use in the rubber industry; examples of such pigments are monolite yellow and monolite red.

A consideration will be made of the method of employing the water soluble dyestuffs, which are far more numerous than the insoluble ones, in the coloring of rubber. The obvious way is to convert them where possible into lakes or insoluble colored compounds. The two most important processes of lake making are (1) precipitating an insoluble salt of the soluble dyestuff upon a suitable white pigment, known as the "lake-base" and (2) employing a mineral earth which absorbs certain dyes from aqueous solution.

A word of warning should be added here with regard to lakes prepared by absorbing colors upon mineral earths: the commonest absorbent is a mineral known as "green earth," which unfortunately more often than not contains traces of manganese, which renders its use in rubber colors highly undesirable.

It has been suggested that the rubber compounder could to all intents and purposes prepare his own lakes by simply pouring a solution of the dyestuff over clay, but there appear to be three serious objections to this procedure; firstly, it is not easy to balance the amount of color and clay to give a pigment fast to water; secondly, the resulting dried clay mass is in some cases far from easy to grind; and thirdly, the rubber man prefers to purchase satisfactory colors from the color manufacturer.

Mention should also be made here of the use of special vehicles for conveying the color into the rubber, such as the various substitutes and synthetic resins. Unfortunately white substitute and most of the synthetic resins do not actually dissolve in rubber, and hence are not ideal vehicles for this purpose.

Briefly, the testing of rubber colors may be classified thus:

(1) Moisture content.

(2) Fineness (*a*) by lightly brushing the color with a camel-hair brush through standard I. M. M. sieves, (*b*) by examination under the microscope.

For the examination of the color after dispersion in the rubber the most convenient apparatus to use is one which was brought to the writer's notice by Hauser. It consists of a brass cell into which is placed the microscope slide containing the uncured mix. By screwing up the cell the mix is nipped out to the necessary thinness without damage to the glasses, which are supported by the walls of the cell except for the small hole through which the observation is made. The cell containing the slide can be placed in an oven to follow the effect of the cure upon the color.

(3) Freedom from water soluble color. This is difficult to determine, since there

is no sharp distinction between water soluble and insoluble colors. A practical standard must be adopted.

(4) Shade. The shade should agree with that of the standard both in full and tint shades in the standard test mix, which for convenience may be taken as a zinc oxide mix containing 50 per cent pale crepe rubber. When exact matching is important the shades should be compared under the mercury vapor lamp, in the light of which differences can be detected which are not apparent in daylight. In no circumstance should the comparison be made until the rubber is cold.

If a color such as monolite red is incorporated in the test mix in gradually increasing proportions it will be found that there is a more or less well-defined concentration above which there is little increase in shade for a given increase in pigment. The shades at and above this concentration are described as "full" shades and those below as "tint" shades (the "undertone" of the paint trade).

(5) Strength. The strength should be determined by tint shades only, as differences are not so apparent in full shades.

(6) Light fastness. Exposures should be made as far as possible under service conditions and in no case under glass.

If it is desired to use the mercury vapor lamp, a test against daylight should first of all be made to ensure that the behavior of the color under the action of this light is normal. A color which bleaches in daylight may apparently darken or at least show little change under the mercury lamp.

One or two colors change in shade under the influence of sunlight, but return to their original shade on the removal of that influence, thus spirit yellow IV changes from a bright yellow to a deep orange-yellow. This is not a heat effect, although certain colors are known which are thermotropic, thus lake red C changes from a yellowish red to a bluish red under the influence of heat, and returns to its original shade on cooling. This latter effect has given rise to great consternation of mind on the part of the proofer, who witnesses for the first time the effect of the hot plate upon a proofing containing this color.

(7) Bleeding in rubber. This can conveniently be tested by curing a test mat containing a white sector.

(8) Practical conditions. The color must be tested under the exact conditions under which it will be used. This is after all the only criterion of its usefulness for a particular purpose.

The following experiments were made to find the effect of organic colors (two typical inorganic colors, namely ultra-marine and red oxide of iron, were included for comparative purposes) upon the aging of rubber.

The basic mix employed contained: pale crepe rubber, 100 parts; zinc oxide, 6 parts; lithopone, 22 parts; catalpa, 50 parts; magnesia, 2 parts; sulfur, 2 parts; tetraethylthiuramdisulfide, 0.375 part. The proportion of the following dyestuff or pigment added was adjusted to give a full shade, and is expressed as a percentage on the above mix; ultramarine, 6; red oxide, 6; Vulcafor red, 2; Vulcafor yellow G, 2; Vulcafor orange, 2; Vulcafor scarlet, 2; Vulcafor green, 2; Vulcafor blue, 0.75; Vulcafor yellow I, 0.35; Vulcafor yellow IV, 0.35; Vulcafor red III, 0.35.

The cure in all cases was 10 minutes in the press at 40 lb. per sq. inch. The sheets were 2 mm. thick. The sheets were tested 24 hours after curing, after 14 days in the Geer Oven at 70° C., after storage in the dark for six months, and after exposure (both sides) in the open for six months.

The figures given in Table I are the average results obtained by the breaking of 12 dumb-bell pieces in each case. The general procedure in the testing was that recommended by the Physical Testing Committee of the Division of Rubber Chemistry of the American Chemical Society.

It will be seen that the colors appear to have had a bad influence upon the heat aging, but a good effect upon the normal aging of the rubber.

Further experiments (see Table II) were therefore made with similar compounds, but this time with the addition of 1 per cent on the rubber of a chemical anti-ager (Nonox). Unfortunately, time did not allow of an equal time of exposure, but parallel experiments in the Geer oven demonstrated that on the whole the colors now had little if any effect upon the heat aging of the rubbers.

TABLE I

EFFECT OF AGING UPON RUBBER CONTAINING ORGANIC COLORS

Name	Before aging			14 days at 70° C.			Storage in dark for 6 months			Exposed for 6 months		
	T_{400}	T_B	E_B	T_{400}	T_B	E_B	T_{400}	T_B	E_B	T_{400}	T_B	E_B
Blank	61	225	700	39	105	650	87	262	690	66	193	680
Vulcafor red	62	203	690	23	49	600	85	241	660	68	213	680
Vulcafor scarlet	62	211	700	30	34	460	86	250	670	79	242	700
Vulcafor orange	54	209	710	29	66	620	77	245	680	64	221	710
Vulcafor yellow G	69	204	680	30	38	550	92	258	640	83	230	650
Vulcafor green L	65	220	700	32	34	450	95	253	650	82	255	710
Vulcafor blue	64	213	710	31	52	580	94	249	660	79	251	700
Vulcafor red III	38	231	760	21	68	650	54	264	740	52	269	740
Vulcafor yellow I	37	227	780	18	61	650	50	258	740	49	231	750
Vulcafor yellow IV	42	249	780	21	63	660	65	264	720	64	255	730
Iron oxide	63	195	680	38	86	630	97	249	660	87	242	670
Ultramarine	63	198	680	33	72	610	79	231	675	64	167	650

TABLE II

THE EFFECT OF AN ANTI-AGER UPON THE AGING OF RUBBER CONTAINING ORGANIC COLORS

	Before aging			14 days at 70° C.			Storage in dark for 3 months			Exposed for 3 months		
	T_{400}	T_B	E_B	T_{400}	T_B	E_B	T_{400}	T_B	E_B	T_{400}	T_B	E_B
Blank	62	237	730	64	213	690	77	275	655	71	253	710
Vulcafor red	57	218	730	71	208	670	71	251	710	67	246	700
Vulcafor scarlet	55	219	750	65	184	680	67	240	710	66	244	705
Vulcafor orange	63	234	735	68	204	680	76	268	690	71	253	720
Vulcafor yellow G	60	231	720	71	205	680	75	273	710	74	256	710
Vulcafor green L	57	215	720	66	190	680	71	249	710	70	247	710
Vulcafor blue	56	227	740	62	201	680	75	268	720	69	257	710
Vulcafor red III	59	236	735	73	221	680	75	263	710	69	266	725
Vulcafor red III + stearic acid	33	233	790	42	215	760	58	271	720	45	250	770
Vulcafor yellow I	60	236	740	70	205	680	75	274	710	73	265	710
Vulcafor yellow I + stearic acid	35	244	800	41	202	760	51	270	750	44	247	760
Vulcafor yellow IV	58	229	740	71	214	690	72	264	710	69	259	720
Vulcafor yellow IV + stearic acid	31	233	820	43	218	770	51	258	760	45	254	770
Iron oxide	63	226	720	72	200	670	75	253	710	70	249	710
Ultramarine	68	216	710	75	219	660	81	256	680	75	237	680

TABLE III

Color	Exposed 6 summer months T. E. T. with 1% Nonox on the rubber	Exposed 6 summer months E. T. T.	Exposed 7 summer months D. P. G.	Exposed 7 summer months D. O. T. G.	Exposed 12 months T. E. T.	Exposed 3 hours 12 in. from a 6-in. mercury lamp, T. E. T.
Vulcafor red	S	S	S	S	S	S
Vulcafor scarlet	S	S	S	S	S	S
Vulcafor orange	S	S	S	S	S	S
Vulcafor yellow G	S	S	S	S	S	S
Vulcafor green	S	S	S	S	S	S
Vulcafor blue	S	S	S	S	S	S
Vulcafor red IV	L. d.	L. d.	D	D	D	M. d.
Vulcafor yellow I	L. d.	S	L. d.	L. d.	D	D
Vulcafor yellow IV	D	D	D	D	M. d.	D

S = same. D = darker. L. d. = Little darker. M. d. = Much darker.

In the experiments marked "Color plus Stearic Acid" the dyestuffs were previously dissolved in two parts of stearic acid.

Sheets of rubber cured with (1) tetraethylthiuramdisulfide, (2) diphenylguanidine, (3) di-*o*-tolylguanidine, and (4) tetraethylthiuramdisulfide and Nonox were exposed for various times, and the results of the effect on the color are summarized in Table III.

The application of organic colors may be considered under three main headings: latex, soft rubber, and ebonite.

LATEX.—The coloring of latex is naturally assuming greater importance with the development of processes for its commercial application.

Broadly speaking, when the latex is to be vulcanized at or slightly above the ordinary temperature by means of super-accelerators, almost any dyestuff may be employed to color it, provided the dyestuff carries a negative electric charge, and hence does not bring about coagulation.

Whether or not it is economical to employ water-soluble dyestuffs in the coloring of latex will depend upon the use to which the latex is to be put: generally speaking, when the serum is to be separated from the rubber by any means other than evaporation, it will be found to be uneconomical owing to the loss of color in the water. When it is intended to compound the mix in the latex itself, then by the use of a suitable filler, such as China clay, the unbound water soluble color may be fixed and the finished goods will not require to be surface washed to remove any free color, in fact this appears to the author to be the only case in which the rubber technologist has any real practical interest in the absorption of water soluble dyes by clays. Of course, the pigment colors and lakes may be employed in such water compounded mixes, but for this purpose especially, they must be in a fine state of division since the dispersing action of milling in a plastic (in this case rubber) is now absent. In practice, of course, the absence of milling usually gives rise to the necessity of putting the pigment through one of the mechanical colloid mills.

There is another interesting application of organic dyestuffs to the coloring of latex, and that is the use of vatable dyestuffs. These compounds are insoluble in water, but become soluble when reduced to their leuco compounds by any of the common reducing agents. The soluble form of the dye is mixed with the latex, which is then agitated in air when the dyestuff oxidizes to its insoluble form upon the rubber particles.

In the more recent development, namely, the electro-deposition of rubber, still further limitations are encountered, since now not only must the color be fine enough to give uniform coloration to the eye, but it must be fine enough to travel in the electric field and be deposited with the rubber at the anode; in other words, it must possess a particle size comparable with that of the rubber particle in latex. It is now necessary to revise completely the old ideas of fineness, since what was formerly considered to be of excellent fineness must now be regarded as coarse, in fact it is necessary to prepare the colors in colloidal solution. In some cases by adjusting the conditions of the reaction the pigments may be prepared in the colloidal state, or at least in a state of sub-division approaching that state, and after the removal of the inorganic impurities it is only necessary to add a suitable protective colloid in order to maintain the pigment in that state; in other cases this is not possible and it is necessary to resort to other methods of dispersion. The method which will immediately suggest itself is the colloid mill, but it is a remarkable fact that with many of the organic pigments the colloid mill will only reduce them to a certain state of division, quite fine enough for ordinary water compounding, but not fine enough for electro-deposition, and repeated passage through the mill will not alter this state of affairs.

The main requirements of pigments of the electro-deposition process are therefore (1) that the pigment should have a negative electric charge and (2) that it should have a particle size comparable with that of latex and be free from coarse particles, which would settle out in the bath instead of being deposited on the anode.

The colors for this purpose can be tested by the usual methods, such as by placing the emulsion under distilled water in a U-tube containing electrodes, or by placing a drop on a microscope slide fitted with tin foil electrodes (method of Cotton and Mouton).

SOFT RUBBER.—The whole key to success in the production of brightly colored rubber is the use of accelerators. In fact, one of the most difficult problems of the rubber colorist when an accelerator is employed is to find a range of colors which are completely fugitive in a white mix during cure, in other words, a range of marking colors for distinguishing between uncured white mixes. A few of the basic dyes will bleach out during the cure, but will redevelop again after standing for a few hours.

It will be seen, therefore, that almost all of the organic colors are more or less fast to the curing conditions of rubber in the presence of a super-accelerator. They do not, however, all constitute good rubber colors.

Organic rubber colors can be divided into three main classes: (1) soluble in rubber, (2) an intermediate class slightly soluble in rubber, (3) insoluble in rubber. The first two classes are purely organic dyestuffs, but the third class may be divided into two groups: (*a*) organic pigments, and (*b*) lakes.

(*1*) *Soluble Colors.*—The most common colors belonging to this class are the reds and yellows, but it must not be supposed that blues and violets are lacking. Such colors exist and are exceptionally fast to light, but perhaps they are rather too expensive for everyday use.

These colors are possessed of one great failing as a class, and that is that not only do they dissolve in rubber, but they crystallize from rubber. To use them successfully, it is necessary to determine their solubility at the ordinary temperature in the particular mix and not to exceed this concentration. In ordinary pale crepe, this figure is very low indeed, about 0.3 per cent. If this figure be exceeded, the dyestuff will crystallize out and the crystals will slowly migrate to the surface of the rubber with the production of a dull brown "bloom" (in the case of Vulcafor red III). Certain substances, to which reference will be made later, tend to delay this crystallization; but still more remarkable is the fact that certain substances, which one would expect to be quite inert in this respect, tend to accelerate it. Thus, if iron oxide is added to a mix containing Vulcafor yellow I, in such concentration as to be perfectly stable under normal conditions, the yellow will soon commence to "bloom" from both the uncured and cured rubber.

The incorporation of these colors into the rubber is often attended with difficulties due to the big difference in solubilities at milling and curing temperatures. A small speck of dyestuff may remain undissolved after the milling, but during the curing will dissolve and produce a darker colored spot, which owing to diffusion becomes a regrettably large blot. Various attempts have been made to overcome this difficulty, such as prolonged grinding of the color with some white pigment such as *blanc fixe*, but with only partial success. There is, however, a method by which not only can easy incorporation be secured, but also a slight improvement in the risk of "blooming," and that is first of all to convert these colors into their stearates by melting them with about twice their weight of crude stearic acid. The fused mass on cooling may be roughly broken up and milled into the rubber, into which it will pass with the greatest ease and perfect solubility. A mixture of

stearic acid and common rosin has been suggested, but it appears to offer little if any advantage over crude stearic acid.

The ideal solution to this problem would be to discover a protective colloid which would prevent the growth of the color particles, but such protective colloids for substances which crystallize easily are difficult to find.

Naturally rubber soluble colors have great limitations in use, because they bleed from one piece of rubber to another, or into paper placed in contact with it. They are not, of course, fast to naphtha or most of the organic solvents. They find application, however, for special purposes such as, for instance, marking the position of valve patches (English Patent 246,067).

(*2*) *Slightly soluble in rubber colors* are unfortunately comparatively few in number. Probably the most characteristic members of this group are such colors as Vulcafor yellow and Vulcafor scarlet. These colors are not sufficiently soluble to bleed from one piece of cold rubber to another. Under certain conditions when the rubber is hot it is true that these colors show this tendency. Under no conditions will these colors bleed from rubber to packing paper, however long the storage. For most purposes this class of colors is ideal, since they need not necessarily be in a fine state of division in order to secure dispersion, they contain the maximum amount of dyestuff and the minimum amount of filler, and when being milled into the rubber they show no tendency to fly.

(*3*) *Insoluble in rubber colors* may be subdivided into the organic pigments and the lakes made from water-soluble organic colors. It is difficult to decide in some cases whether a given organic pigment should be classified as belonging to Class 2 or Group (*a*) of Class 3. Generally speaking, if it is possible to use an organic pigment as such it will be found to be more easily dispersible in rubber than the corresponding lake, although for certain purposes the lake is to be preferred. For example, in the open steam cures, many of the organic pigments show a tendency to bleed from the surface into the cloth wrapper, whereas the corresponding lake would not do so. It should not be assumed that such discolored wrappers are spoilt, since there appears to be little tendency for the reverse to take place. In the case of open-air cures, with or without pressure, the straight pigments are perfectly satisfactory. The same remark applies to press cures.

Two special applications of organic colors, for the production of transparent rubber and jazz effects, will be considered.

Transparent Rubber.—The pale crepe to be used for this purpose should be as free as possible from suspended matter, and great care should be taken to ensure that the rubber and compounding ingredients are perfectly dry, or turbidity will result during the cure. The accelerator and activator should be selected with a view to perfect solubility in the rubber. Zinc or cadmium stearates are perhaps the safest activators, since there is less danger of undissolved particles than when the oxides are employed. Of the two, the cadmium compound is the most satisfactory, since larger amounts may be used without fear of cloudiness, but it possesses the disadvantage of imparting an amber color to the rubber. There is, however, no objection to this color when reds or browns are required. A minor point to be kept in view, when employing cadmium oxide or stearate, is that these substances have a slightly greater activating effect than the corresponding zinc compounds, and therefore a slight reduction in the time of cure is recommended.

With regard to the most suitable colors, the ideal ones should be perfectly soluble in the rubber and used at such concentration that there is no fear of any separation or blooming on storage. Rubber soluble colors are, however, not absolutely essential, since certain colors which give in rubber colloidal dispersions which do not aggregate may be employed with success.

Another novel and interesting effect which requires the same technic is the production of rubbers with metallic lusters. These effects may be obtained by compounding aluminum powder into white transparent rubber for a silver effect or into transparent rubber colored with Vulcafor yellow I for a gold effect. The latter procedure is far safer than employing any of the bronze powders which may contain copper. It is, of course, possible to obtain aluminum powders, upon which transparent lakes have been formed and which have the appearance of gold or copper, but many of these colors are fugitive to vulcanization.

Jazz Effects.—In many of the early attempts to produce marbled and jazz effects, the colored pigment was simply dusted upon the mix as it passed through the calender. Needless to add, the result was neither pleasing nor practical. The best effects can only be obtained by the partial mixing of different portions of the basic rubber compound into which the various colored pigments have been properly incorporated.

There are three important considerations to be kept in mind in the production of these effects. (1) The colors employed must be practically insoluble in rubber, both in the cold and during the cure. In steam cured goods, the selection of pigments is still further narrowed down, since some colors which do not bleed in press cures will do so in open steam. (2) The various portions of colored mix should be of the same plasticity when put through the rolls, producing the jazz effect, and (3) the degree of mixing must be just sufficient to give the effect and no more, or dull patches will result from the blending of complementary colors.

A novel method of obtaining a far more natural marble pattern is to split the rubber as it leaves the calender upon which the jazz mixing has been effected (U. S. Patent 255,017). Incidentally it may be mentioned from the aesthetic point of view that a pleasing jazz will always be found to contain a predominance of white or some bright color, such as yellow. With regard to the most suitable accelerators for use in the curing of colored soft rubbers: in press-cured goods a thiuram accelerator should be employed, and for use in dry heat preferably an accelerator of the type of zinc diethyldithiocarbamate. Quite satisfactory results can be obtained with most of the slower accelerators such as di-*o*-tolylguanidine, except in the case of one or two colors of the vat dyestuff class, which appear under certain conditions to be partially reduced during the cure. In such cases quite excellent results may be obtained by the substitution of aldehyde-ammonia as the accelerator. The only class of accelerators which should be definitely ruled out is the resin type made from aromatic amines, since these accelerators discolor the rubber.

A few of the organic rubber colors exert a feeble accelerator action which can be neglected in an accelerated mix, except perhaps in the case of Vulcafor yellow IV which even in the presence of such an accelerator as tetraethylthiruamdisulfide involves a shortened cure.

Ebonite.—In the coloring of ebonite there is the obvious difficulty of covering up its natural brownish black color: this involves the use of a large proportion of color. It is true that this color can first of all be covered by the use of a white pigment such as lithopone, but then it is necessary to overcome the hiding power of the white pigment, and furthermore the introduction of the inorganic pigment tends to give rise to a stonelike ebonite. In most cases the brightest results can be obtained by the correct balance of both white pigment and color. In fact, in the case of the darker colors the use of a white pigment is essential, since at the necessary concentration these colors are in themselves very dark. With the paler colors, however, such as yellow or orange, quite bright products can be obtained in the absence of inorganic pigments with consequent improvement in physical properties.

In the successful production of colored ebonite it is necessary to balance the three

factors of time, temperature and sulfur. If it is intended to work at comparatively high temperatures such as steam at a pressure of 50 pounds per square inch, the key to success is to keep the sulfur down to a minimum, which may be taken as about 30 parts of sulfur per 100 parts of rubber after due consideration has been paid to any sulfur which may be absorbed by any other substance in the mix. It is unfortunate from the point of view of colored ebonite that the action of accelerators in its production differs fundamentally from their action in soft rubber, inasmuch as the accelerator has no effect upon the physical properties of the vulcanizate, and hence the sulfur cannot be greatly reduced. The accelerator merely speeds up the inevitable result. Their beneficial effect consists in either reducing the temperature of the cure or in shortening the time. If powerful accelerators are not used carefully they actually do more harm than good in the production of colored hard rubber, since under certain conditions they tend to generate sulfuretted hydrogen which, apart from the harmful effect of the resulting microporosity upon the ease of polishing of the product, actually tends to destroy by reduction the colors. Since many of the best ebonite colors, especially the vermilion substitutes, are of the class of vat dyestuffs, this generation of a reducing gas is especially harmful. It can, however, be avoided by employing a well regulated rise in curing temperature.

In thick layers or masses of accelerated mix, this generation of gas may become sufficiently powerful and spontaneous to take on the character of an explosion, and cases are known where quite heavy presses have been completely disrupted by this effect.

A typical bright reddish orange hard rubber suitable for, say, fountain pen stocks may be made from the following mix: rubber, 100 parts; Vulcafor orange, 120 parts; magnesia, 4 parts; sulfur, 40 parts; Vulcafor resin, 4 parts. The cure is twenty minutes' rise to 40 lbs. per square inch, and 90 to 105 minutes at that pressure.

In the low temperature production of hard rubber, it is found that time of cure and proportion of sulfur have practically no effect upon the brightness of the result. Thus in a hard rubber cured at or below the temperature of boiling water the sulfur can be increased to over 100 parts per 100 parts of rubber without any detrimental effect upon the shade. On the whole, less color need be employed and brighter results can be obtained with low temperature cured hard rubber. In fact it is an excellent process for the production of brightly colored hard rubber jewelry, such as beads.

A typical low temperature "modified" hard rubber of extreme brightness and capable of taking a very high polish can be made from the following mix (Stevens, English Patent 269,693): rubber, 100 parts; zinc oxide, 20 parts; Vulcafor red, 60 parts; sulfur, 100 parts; zinc diethyldithiocarbamate, 20 parts. The cure is about 15 hours at 95° C.

Generally speaking, the best ebonite colors are insoluble colors, especially those belonging to the vat dyestuff class; but here again these colors vary considerably from one to another, probably depending upon their ease of reduction to the leuco compounds by hydrogen sulfide. The rubber soluble colors are on the whole unsuitable for ebonite, since not only do they change in color during vulcanization, but they tend to cause evolution of hydrogen sulfide. In all cases the surface must be carefully protected against the action of live steam. Unlike soft rubber, the surface of ebonite cannot be protected by mere cloth wrapping. It is true that this destructive action is only a surface effect which can be removed in the final polishing operation, but in most cases it is unfortunately too deep-seated to allow of the use of certain colors, such as Vulcafor orange, in the production of dental plates, which are, of course, to all intents and purposes cured in open steam, since the plaster

mould is not steam tight. Certain vat colors, however, have been used successfully in the coloring of dental ebonites.

It appears to be difficult to produce satisfactory colored ebonite by moulding a mixture of ordinary ebonite moulding powder and color; but satisfactory results, however, can be obtained when the moulding powder is made from properly prepared colored ebonite dust. It was at first thought that the failure was due to the coarseness of the ebonite dust or of the color with which it was mixed, but trials with specially prepared dust upon which dispersed colloidal pigments were deposited also gave very dull results. By the addition of certain resins better results may be obtained, but the resulting product can hardly be called ebonite.

This leads to another interesting substance, namely, the mixed ebonite and synthetic resin. It has already been mentioned that incompletely polymerized phenol-formaldehyde resins (resoles) cannot be used in soft rubbers, owing to their extreme retarding effect upon cure. With hard rubber such resoles, provided they are free from phenol, can be employed, but here again it will be found necessary to give a longer cure than in their absence. This immediately offers a further method of introducing color into the ebonite. It is possible to mill completely hardened powdered resin into the uncured mix containing the color, just as it is possible to do the same thing with, say, powdered quartz, and in this way the resin has no effect upon the cure. The intimate dispersion may not, however, be obtained in this way, as the ordinary phenol-formaldehyde resole itself is not soluble in rubber, and hence is not easily dispersed. When such mixtures are cured, it is essential to use the hydraulic press, since the evolution of the few per cent of water during the final polymerization of the resin leads to microporosity in open cures. Even when the press is employed it is often difficult to obtain a product free from microporosity.

In conclusion it is safe to affirm that organic colors have made possible the production of bright effects which have done so much to popularize the use of rubber in many new directions. It is not expected, however, that these special colors will replace the old standard inorganic colors for many purposes in which brightness is not an important factor.

The author wishes to express his thanks to the British Dyestuffs Corporation, Ltd., in whose Rubber Service Laboratory the work was carried out, for permission to publish the results embodied in this paper, to the staff of that laboratory for the preparation of samples of colored rubber exhibited at the meeting, and to Mr. W. F. Smith for his help in carrying out the lecture experiments.

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Dispersoidological Investigations. XXIII

Contributions to the Dispersoidology of Rubber. Part I—The Structure of Jellies and of Other Coagula of Ammonia-Preserved *Hevea* Latex and *Hevea* Vultex

P. P. von Weimarn and Collaborators

PREFACE

In the course of my dispersoidological investigations of natural silk,[1] I succeeded in obtaining it in such a highly elastic state as may truly be called a rubber-like state. However, the highly elastic state of silk is not a lasting one; sometimes it persists only for several minutes, sometimes for several hours, seldom does it last for several days and rarely in the extreme for about a week. Thus the rubber-like state of silk is a temporary state; but the high elasticity of rubber itself is also not everlasting. Evidently in both these cases there exists only a great quantitative difference in the duration of the existence of the highly elastic state under consideration.

The ultramicroscopic study of the structure of separate threads of silk in different stages of their swelling, *i. e.*, in different stages of elasticity, has led me to the conclusion that in principle it is possible to obtain in a rubber-like state such disperse systems, the component parts of which are substances quite different in their chemical composition from rubber-hydrocarbons.

May the rubber-like state, under certain conditions, be a state universally possible for disperse systems composed of any substances, or not?

I answer this question in the negative, because for the imparting to a system of the rubber-like state, the substances composing such a disperse system must possess special properties.

One of these properties is a special distribution of the intensities of vectorial forces in vectorial fields around the molecules of substances composing the disperse system which, under certain conditions, is able to possess a rubber-like state.

These vectorial fields in two regions opposite in direction must possess greater intensities than in all other regions of the same vectorial field. The particles with such vectorial fields will evidently produce systems with a "fibril cleavage."[2]

But this property is not alone sufficient for the imparting to a disperse system of the rubber-like state.

As I have formerly stated: "A system possessing the high elasticity of rubber must have the following structure: (1) The primary structure elements of such a system must possess the form of spirally curled fibrils: (2) The interfibril dispersion medium must be extremely viscous (plastic) and permit the fibrils, after the stretching out of the system, to become more or less straightened, as well as to become curled after the system has been released from tension.

The primary structure elements may of course give rise to secondary, tertiary,

[1] *Reports of the Imperial Industrial Research Institute of Osaka*, **7**, No. 8 (March, 1926).

[2] *Reports of the Imperial Industrial Research Institute of Osaka*, **8**, No. 6, 23 (June, 1927).

Plate I

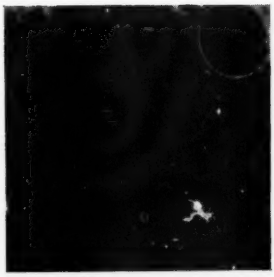

Fig. 1—× 475

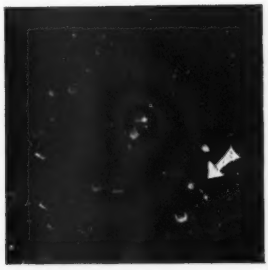

Fig. 2—× 475

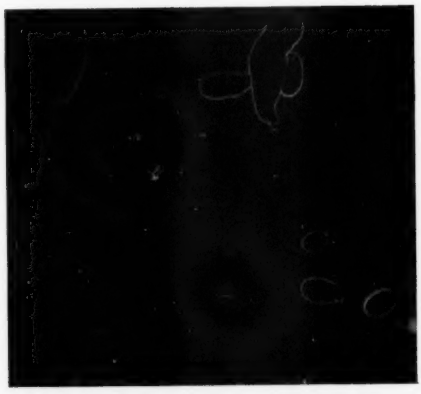

Fig. 3—× 475

Fig. 4—× 475

Fig. 5—× 1140

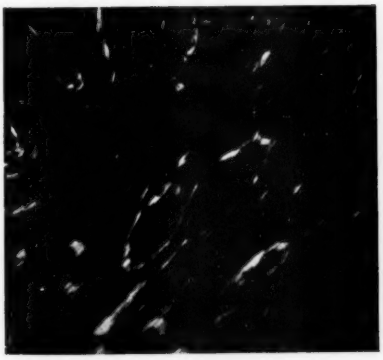

Fig. 6—× 475

Fig. 7—× 475

etc., structures; but all these structures must possess the possibility found in their primary structure elements of becoming spirally curled after the system has been released from tension, because, as I am convinced, only through the straightening and curling of the spiral structure are achieved those great extensions and contractions which are appropriate to rubber.

The interfibril viscous dispersion medium may have the consistency of a plastic oil or that of a jelly, but in the case of its being a jelly, it must during the stretching out of the system be able to dispergate into a plastic condition."[3]

I entertain no doubts as to the possibility of obtaining in a durable rubber-like state disperse systems composed of substances of a different chemical composition from rubber hydrocarbons, *e. g.*, systems composed of proteins or carbohydrates. However, except by a lucky chance, I do not consider it an easy task.

In order to facilitate the future solving of this problem, I undertook the dispersoidological investigations of natural rubber. The description of a part of this work is presented in the following pages.[4]

THE SHAPE, DIMENSIONS, STRUCTURE AND CONSISTENCY OF AMMONIA-PRESERVED *HEVEA* LATEX AND *HEVEA* VULTEX PARTICLES

The Shape of Latex and Vultex Particles

In former days (V. Henri, 1906), it was assumed that the shape of latex particles is either sphere-like[5] or oval; in 1911, Petch[6] established that besides round particles and those with oval contours, there exist in *Hevea* latex particles of egg-like and pear-like shapes, and also particles with tails. Beadle and Stevens[7] have confirmed the observations of Petch. Other investigators[8] (Babilioff, Hauser, Freundlich and Hauser) have also pointed out the difference of shape in latex particles established by Petch.

I investigated ammonia-preserved latex and Vultex by means of an immersion ultramicroscope by Zsigmondy, and by means of a large reflecting condenser with a change-over device for bright field and dark field illumination, and by a dark field condenser A (with azimuth-stop).

In the work with these two pieces of apparatus, a special oil-immersion objective, a $^1/_{12}$, was used with periplanatic eyepieces $\times 12$ and $\times 25$, *i. e.*, the magnification was 1140 and 2375 fold.

Of the above apparatus the second is the most convenient for this investigation, because it affords the opportunity of using different methods for the field illumination (dark-ground, bright field and combined field illumination).

In Fig. A, the contours of particles Nos. 21–25 correspond to those of Vultex[9] particles (see Plate II, Figs. 10 and 11); particles of similar contour are also present in latex (see Plate II, Figs. 8 and 9).

In the case of latex it offers no difficulty to prepare by artificial means large

[3] *Reports of the Imperial Industrial Research Institute of Osaka*, **8**, No. 13, 79 (November, 1927).

[4] For further results presented in a concise form, see *Bulletin of the Chemical Society of Japan*, **3**, 157 and following (1928).

[5] See, *e. g.*, F. W. Hinrichsen und K. Memmler, "Der Kautschuk und seine Prüfung," p. 12 (1910). Verlag von Hirzel, Leipzig.

[6] T. Petch, "The Physiology and Diseases of *Hevea Brasiliensis*," p. 18, London, 1911; see also Clayton Beadle and Henry P. Stevens, *Kolloid-Z.*, **13**, 215 (1913).

[7] Clayton Beadle and Henry P. Stevens, *Kolloid-Z.*, **13**, 215 (1913).

[8] For reference see E. A. Hauser, "Latex" (1927). Verlag von Theodor Steinkopff, Dresden.

[9] E. A. Hauser ("Latex," 129) writes: "Am augenfälligsten ist hierbei die Feststellung, dass im vulkanisierten Latex die Teilchengestalt im allgemeinen der Kugelform nähe kommt als im Rohlatex." Neither the photomicrograph in ultra-violet light, taken by Henry Green (Plate III, Fig. 13) nor my own photoultramicrographs (Plate II, Figs. 10–11) are in accord with this statement.

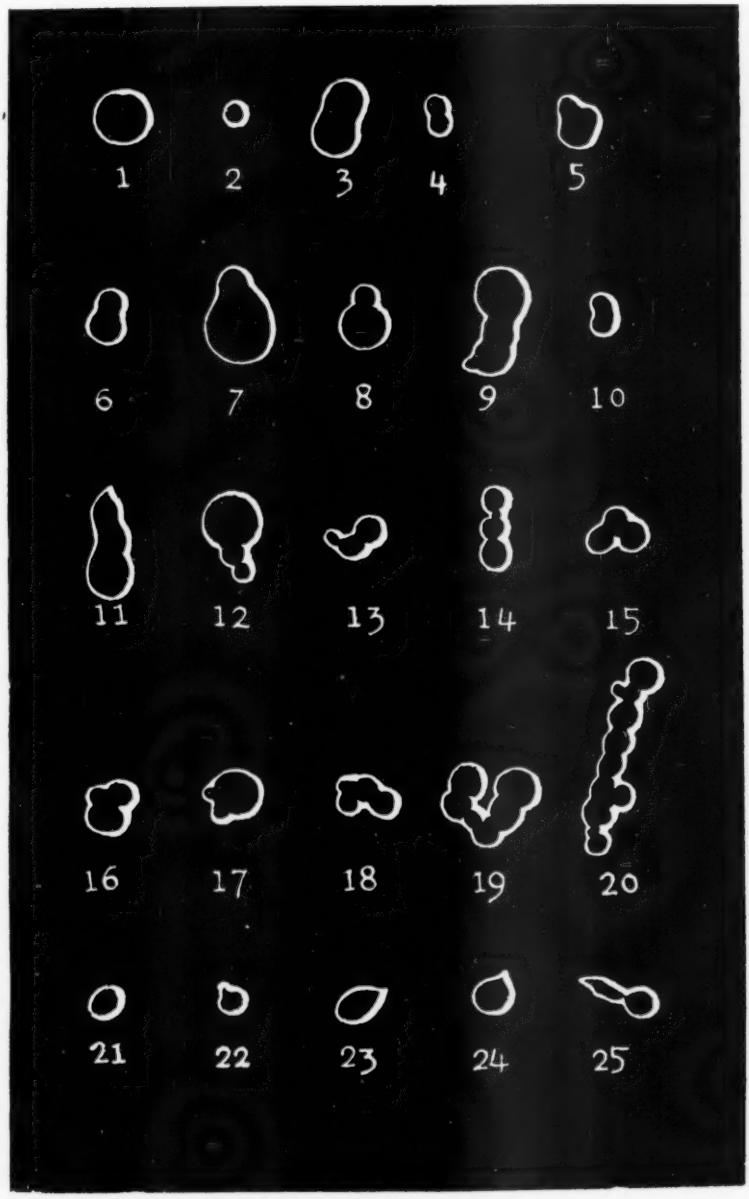

Figure A—Magnification About 2400 Fold

particles, the shape of which differs considerably from spheres. In order to obtain such particles, the latex is diluted with water (1:300 or 1:200). After boiling for several minutes, the mixture is allowed to stand still in a tall cylinder at room temperature. The samples of latex for the microscopic investigation must be taken from the upper layers.

In Fig. A the contours of the particles Nos. 1–20 correspond to those of particles found by me in upper layers of diluted latex (after boiling it for several minutes) and after allowing it to stand still during several days at room temperature (see Plate III, Figs. 16–20).

In Fig. A (also in Figs. 16–20, Plate III) it is easy to observe that the pear-like particles, those with tails and the like, were formed by the flowing together and deformation of the sphere-like particles (Nos. 1–2, Fig. A).

The original form of *Hevea* latex particles is that of spheres, but by deformation during movement in plants of separate particles, as also of their small gatherings, there are produced the shapes of particles different from spheres.

Beadle and Stevens,[10] already in 1913, observed the flowing together of particles in ammonia-preserved *Hevea* latex.

Pear-like particles, those with tails and the like, are not peculiar only for latex, but they are characteristic of many emulsions, the surfaces of whose drops are covered with plastic-solid membranes.[11]

For instance, by mixing on an object glass a drop of immersion oil with a drop of concentrated aqueous NaI solution, it is possible to obtain relatively highly disperse systems, as well as systems of a coarse dispersity, both containing pear-like particles, oblong ones and those with tails.

Figures 1–7 in Plate I (in Fig. 7 are seen the so-called "oily stripes") are clear illustrations of the shape of these disperse particles.

Of the most interest is a coarse pear-like particle in Fig. 1, and a fine particle with a tail in Fig. 5 (the latter particle was in trembling Brownian movement and therefore gave the impression of being accompanied by its shadow).

A more detailed consideration of these interesting disperse systems (immersion oil + NaI or LiI aqueous solution) does not enter into the program of the present paper.[12]

The Dimensions of Latex and Vultex Particles

The diameter of the largest sphere-like particle which I could observe in the ammonia-preserved latex is 3.5μ; and the greatest dimensions of the longest (with a tail) particle is 6.7μ. These numbers closely correspond to those obtained by Hauser.[13]

The exact smallest dimensions possible to latex particles are ascertained with difficulty; at any rate they do not exceed several tens of mμ.

The preparation of such fractions of latex which in a bright field of illumination seem perfectly homogeneous, *i. e.*, the preparation of really colloidal latex, has been already described in one of my papers.[14]

[10] *Loc. cit.*, p. 208.

[11] All emulsions which are considerably stable in high concentrations contain particles covered with such membranes. Hence I share the point of view of Kaye expressed by him during the discussion of the address of van Rossem, *The India Rubber Journal*, **68**, 1126 (1924).

[12] I wish to point out the very interesting amoebiform movements and the change of shape of certain disperse particles of these systems (follow the direction indicated by a white arrow), which take place when the particles meet any obstacles in their way.

[13] E. A. Hauser, "Latex," p. 56.

[14] von Weimarn, *Bulletin of the Chemical Society of Japan*, **3**, 157 (1928).

Plate II

Fig. 8—× 1140

Fig. 9—× 2375

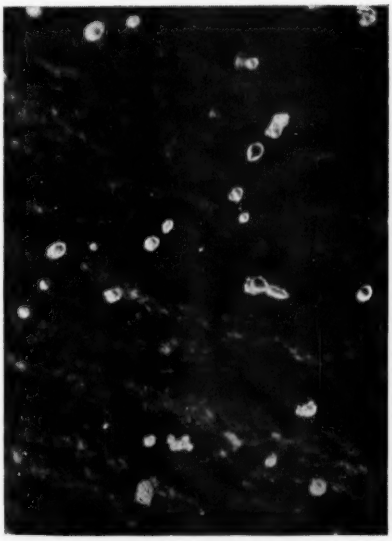

Fig. 10—× 1140

Fig. 11—× 2375

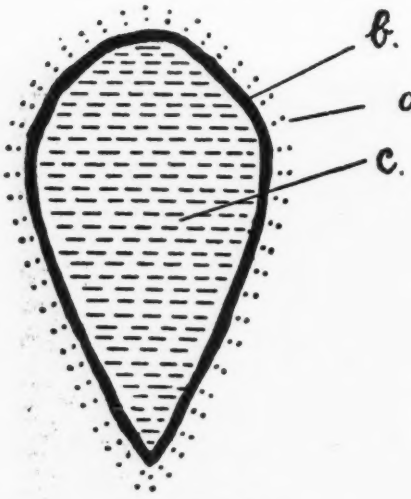

Figure B

Already fifteen years ago Beadle and Stevens[15] admitted the consistency of Heavea latex particles as being similar to that of a thick oil; and that the flowing together of such viscous-liquid drops is prevented by the envelopes of proteins which surround them.

Also Wolfgang Ostwald in the first edition of his book, "Die Welt der vernachlässigten Dimensionen"[16] expressed a similar opinion on the structure of *Hevea* latex.

Freundlich and Hauser[17] arrived at the conclusion (see Fig. B) that the viscous-liquid inner content (*c*) of *Hevea* latex particles is surrounded by two layers; the inner layer (*b*), consisting of gel or of a solid polymer of rubber, presents a substance approaching raw rubber in its consistency; the outer layer (*a*) consists of proteins and resins.

I have already written in another paper[18] that there are no sufficient grounds for assuming that a rubber isospherulite-drop (*i. e.*, a latex particle) is surrounded by any separate "almost solid" (Hauser, "Latex," p. 70) elastic shell of a gel or of a solid polymer of rubber.

As a drop of water in air or in toluene, so also an isospherulite-drop of rubber has a superficial layer, which possesses properties different from those of the inner part; but similarly to the drops of water, which notwithstanding the presence of these superficial layers, coalesce into larger drops, so also the drops of rubber (*i. e.*, latex particles) flow together, if only their plastic-solid envelopes, composed of proteins and resins, will assume a liquid-gelatinous consistency; or if these envelopes be more or less completely taken off from the isospherulite-drops of rubber.

On the ground of my investigations, I hold that the liquid-gelatinous inner contents of *Hevea* latex particles are surrounded by a transitory layer which in its outer section (turned to serum) is composed chiefly of proteins with an admixture of resins (in general, of substances which are in the serum); while the inner section of this layer is in close contact with the superficial layer of the liquid-gelatinous isospherulite-particle of *Hevea* latex.

Figures 22–26 in Plate IV illustrate those changes which are undergone by *Hevea* latex particles and by small aggregates of these particles (see Fig. 21) when a drop of diluted (1:200) ammonia-preserved *Hevea* latex, placed between the cover- and object-glasses, is being uniformly, and with increasing force, squeezed by means of a screw-press.

The changes of shape and the flowing together of latex particles under pressure are objectively demonstrated by the photoultramicrographs in Figs. 22–26.

However, the application of strong pressure becomes needless as soon as a drop

[15] Beadle and Stevens, *Kolloid-Z.*, **13**, 208–209 (1913).
[16] P. 173. Verlag von Theodor Steinkopff, Dresden, 1915.
[17] *Ergänzungsband zu Kolloid-Z.*, **36**, 24–25 (1925).
[18] *Bulletin of the Chemical Society of Japan*, **3**, p. 157 and following (1928).

Plate III

Fig. 12

Fig. 13 (After Henry Green)

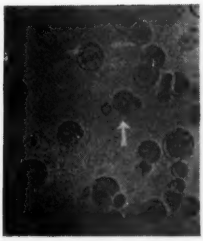

Fig. 14

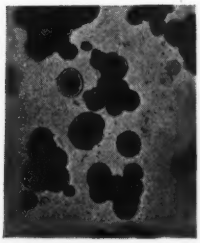

Fig. 15

Fig. 16—× 2375

Fig. 17—× 2375

Fig. 18—
× 2375

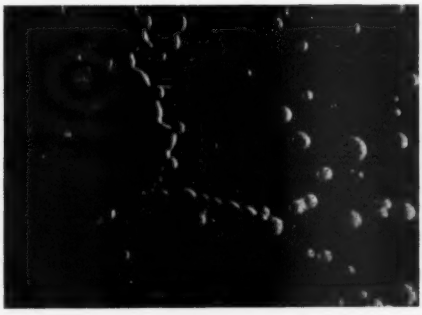

Fig. 19—× 2375

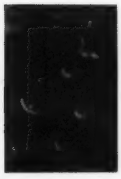

Fig. 20—
× 2375

of latex (diluted 1:200) is mixed with a drop of an aqueous solution of LiI, saturated at room temperature (this solution is a powerful dispergator for proteins).

In this case an abrupt light pressure of the cover-glass upon the preparation suffices to produce a flowing together of latex particles (Fig. 27—the particles of latex and their aggregation before pressure) and the spreading in all directions (Figs. 29 and 30, Plate V) of their liquid-gelatinous contents.

If pressure upon the cover-glass be avoided as much as possible, then the latex particles during the first stage of their coagulation chiefly become stuck together (Fig. 28, Plate V) and only during the subsequent stages (see below) do their rubber contents flow together.

On the basis of his very interesting microscopical investigations in ultra-violet light (see Plate III, Fig. 12) of *Hevea* latex and latex from *Ficus elastica*, Green[19] arrived at the conclusion that *Hevea* latex particles can be forced, by squeezing, to play the rôle of microscopic pulverizers; and these peculiar micro-pulverizers can even produce ultra-microparticles.

I have never been able to obtain such results by squeezing *Hevea* latex particles; by a not too strong pressure of these particles I succeeded in obtaining them in a state similar to that illustrated by Green in another photomicrograph (Plate XI, Fig. 53) and called by him "connecting links."[20]

Now I shall dwell awhile on the question whether the rubber contents of latex particles are homogeneous or not.

The photomicrograph taken in ultra-violet light by Green (Fig. 14, Plate III) leaves no doubt as to the distinctly granular structure of *Ficus elastica* particles. This structure and the presence of central cavities in certain particles of *Ficus elastica* (Fig. 14, Plate III, look in the direction indicated by the white arrow) led me to the conclusion that latex particles are to be regarded as liquid-gelatinous isospherulites.[21]

In *Hevea* latex particles I have had no opportunity to observe microscopical heterogeneity; however, *Hevea* latex particles flattened and deformed by means of a screw-press show under ultramicroscopical investigation a distinct though slight opalescence (it is so fine that it cannot be perceived in the reproduction of Fig. 22, Plate IV, though it is present in the original photoultramicrographs); from the opalescence (Tyndall phenomenon) it is evident that the inner rubber contents of *Hevea* latex particles are ultramicroscopically heterogeneous.[22]

Now I shall proceed to the change in the consistency of latex particles after the vulcanization of latex.

Green, after having investigated vulcanized latex with the Zeiss ultra-violet microscope, arrived at a conclusion (see Fig. 15, Plate III) with regard to the course of the process of vulcanization of *Ficus elastica* latex particles, as follows: "It is apparent that the sulfur passed through the outer shell and fastened itself upon the inner nuclear structure."

Regarding the vulcanization of *Hevea* latex, Green thus concludes: "The only

[19] Ind. Eng. Chem., **17**, 802 (1925).

[20] I suppose that H. Green was brought into delusion by a chance distribution of particles. The increase in number of ultramicroscopic particles under compression of the preparation is quite understandable, because by decreasing the thickness of the preparation there are created more favorable conditions for ultramicroscopic vision. My conclusive opinion on this subject will be formed after the investigation of latex by means of the Zeiss ultra-violet microscope.

[21] von Weimarn, *Bulletin of the Chemical Society of Japan*, **3**, 157 (1928); *Reports of the Imperial Industrial Research Institute of Osaka*, **9**, No. 3, 147–151 (June, 1928).

[22] It may be supposed that in this case, the pressure (squeezing) provokes a decrease in dispersity of particles in the isospherulites of *Hevea* latex; in the case of Green's experiments with *Ficus elastica* particles the same "coagulative" action may be ascribed to ultra-violet rays. Only by further experimenting can it be decided whether these suppositions prove right.

Plate IV

Fig. 21—
× 1140

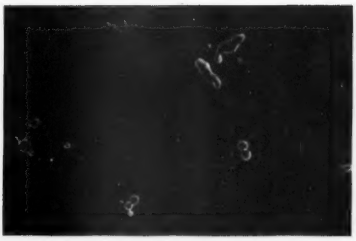

Fig. 22—
× 1140

Fig. 23—
× 1140

Fig. 24—
× 1140

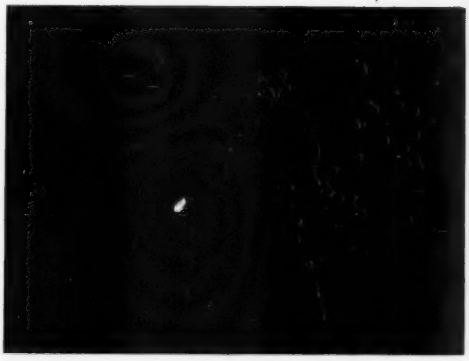

Fig. 25—
× 1140

Fig. 26—
× 1140

definite information that can be derived from figure (see Plate XI, Fig. 54; compare also Plate III, Fig. 13) is that the outer shell of the latex globule takes up sulfur."

It is not easy to understand how from the above conclusion of Green it is possible to deduce[23] that the outer shell of the particles of *Hevea* latex also does not become vulcanized.

From the work of Green only one conclusion may be derived, that all the rubber contents of the particles of latex from *Hevea brasiliensis* as well as from *Ficus elastica* become vulcanized; of course, it does not require any proof that in both cases the protein layer (protein + resins) does not become vulcanized.

In the photomicrographs of vulcanized particles of latex from *Ficus elastica* there are present particles which are entirely devoid of a clear border; it must be borne in mind when commenting upon this photomicrograph that the completeness of absorption of ultra-violet rays is dependent upon the thickness of the layer through which the rays have to pass. During the squeezing of the preparation, the sphere-shaped particles assume the form of more or less strongly flattened lentils.

Vulcanization produces a considerably more viscous consistency in latex particles, but even this great viscosity does not deprive the rubber contents of Vultex particles of the capability to enter into mutual union (to flow together; see below); naturally, this union (flowing together) takes much more time and proceeds with more difficulty than in the case of latex particles.

Owing to their consistency, the Vultex particles with tails (Figs. 10 and 11, Plate II) may be of rectilinear contour; whereas similar latex particles with tails are of a softer contour.

MACROSCOPICAL OBSERVATIONS OF THE GELATINATION AND OF OTHER FORMS OF COAGULATION OF AMMONIA-PRESERVED *HEVEA* LATEX AND VULTEX

Macroscopical Observations of the Gelatination of Latex

I studied[24] the gelatination (and the other forms of coagulation) of latex and Vultex which is brought about by concentration (*i. e.*, by evaporation of water from latex and Vultex) and by the addition of extremely concentrated aqueous solutions of substances which are dispergators for proteins (LiI, LiCNS, $Ca(CNS)_2$, $CaCl_2$, $Ca(NO_3)_2$, etc.; polyphenols, *e. g.*, resorcinol and pyrogallol, thiourea and guanidine thiocyanate); the last experiments were carried out within a wide temperature range, from room temperature up to 170° C.

Whatever the way of gelatination (coagulation) of latex, prior to the assuming by the coagulum (or by the rod of jelly) of the elastic consistency appropriate to rubber coagula towards the end of the gelatination (coagulation) process, the consistency of a latex coagulum passes through successive stages.

These stages are as follows: I. The consistency of the latex becomes viscous; however, it is able to flow slowly. II. A paste or gruel-like consistency. III. A paste consistency; the coagulum when drawn out partially produces sticky elastic threads. IV. An elastic and at the same time plastic consistency; after stretching, the coagulum does not contract to its former length; that is, the coagulum possesses as yet considerable plasticity. V. Highly elastic consistency; the elongations left after a strong extension are minimal.

A coagulum of latex very often in its different parts possesses different consistencies.

[23] E. A. Hauser, "Latex," p. 130.

[24] *Bulletin of the Chemical Society of Japan*, **3**, 157 and following (1928).

Now I shall describe the process of gelatination of latex by the influence of the addition of extremely concentrated aqueous solutions of substances which are dispergators for proteins.

I shall confine myself to only one example: the gelatination of latex, produced by pouring latex into an equal volume of aqueous LiI solution, saturated at room temperature.

All the experiments described below were carried out at room temperature. For experimenting test tubes of 18–20 mm. in diameter were used; into 10 cc. of an aqueous LiI solution were poured very carefully, along the walls of the test tube, 10 cc. of latex; the text tube was vigorously shaken only once; after the lapse of several minutes, the test tube was broken and the rod of jelly cautiously taken out and washed for 3 hours in running water.

The rods of jelly thus prepared were subjected to investigation.

When latex is shaken with LiI solutions there are formed in the upper end of the jelly sticky films which admit of being drawn out into elastic threads; the films stick to the fingers and to the walls of the test tube (the latter occurs if during the shaking the upper part of the contents of the test tube has hit against its walls). The stickiness decreases markedly with time.

After 3 hours' washing, the rod of jelly looks greyish white; it is soft to the touch; its diameter varies between 15–17 mm.

I shall describe the experiment of stretching a rod of jelly just after taking it from the washing bath; the diameter of the rod is 16 mm., the length, 8.5 cm.

The rod permitted extension up to 34 cm., then it broke in one place; during the stretching the rod yielded a turbid serum; the turbidity showing that a part of the latex particles have not coagulated.

The rod when drawn out possesses a silky gloss (fibrous structure). The broken part adheres to the remaining piece of rod. After stretching, the length increases by 4.5 cm. (*i. e.*, the general length is already 13 cm.).

In Fig. C are given contours of another rod of jelly; *a*—the contour of the rod of jelly immediately after washing; the length is about 8 cm., the diameter about 17 mm.; *b*—after 2 weeks' drying in air (the rod was lying on several sheets of filter paper); the length is about 6.5 cm., the diameter—about 10 mm.; *c*—the contour of the rod of jelly after stretching the rod *b* to the length of 37.5 cm. (during this stretching the rod remained unbroken); the rod *c*, when compared with the rod *b*, had the greater

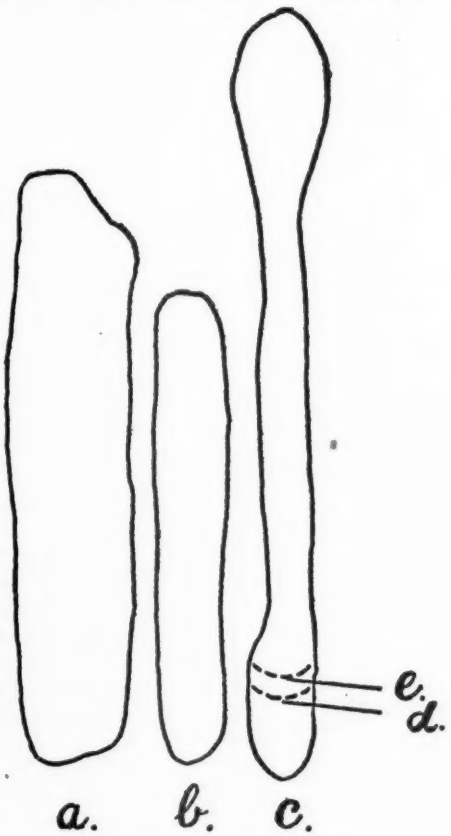

Figure C—Natural Size

length by 4 cm. After 20 minutes from the release from stretching, the rod contracted (line *d*); after the lapse of one hour, its contraction increased (line *e*). On further preservation, the rod *c* became still shorter, but its length did not become equal to that of the rod *b*.

Another rod of jelly (*a* in Fig. D) immediately after washing was moulded, by pressing with the fingers and by rolling between the palms of the hands, into a rod as thin and compact as possible (*b* in Fig. D; after the lapse of 2 weeks, this rod contacted to the length shown by line *c*).

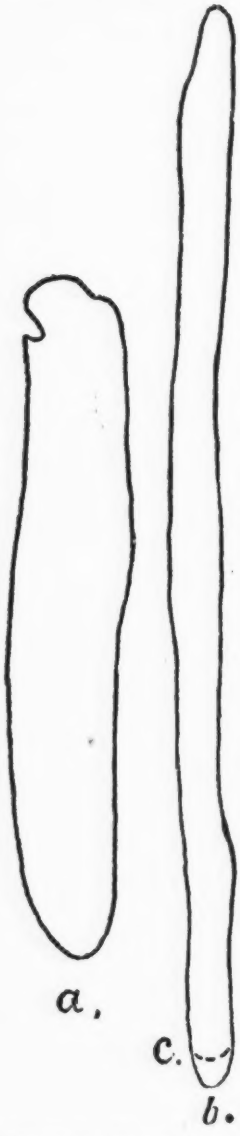

Figure D—Natural Size

During the above deformation of the rod of jelly *a*, the air inclosed therein escaped in the form of bubbles which were covered with the thinnest transparent elastic films of rubber. By increasing the size of bubbles, the film reaches a critical thinness and bursts with a noise.

The fineness of these films, their transparency and impermeability to the air, clearly show without the need of microscopical examination that in these elastic transparent films no integral latex particles are present.

After the lapse of 2 weeks, the rod *b* was stretched to breaking; it broke at the extension to 70 cm.; the persisting elongation equaled about 6 cm.

The rod of jelly *a* in Fig. E, immediately after washing was moulded by the fingers into a plate (about 3 mm. thick) of contour *b;* after 2 weeks the plate contracted to contour *c*. After the lapse of this time the plate was examined for stretching; it broke on reaching the length of about 70 cm. In a drawn out condition, the plate has a silky gloss, and a distinct hatching in the direction parallel to the stretching.

The hatching (in certain places being in the form of oblong cavities, Fig. F, *b*, *c*, and of more or less long inner tubes, section *d*, Fig. F) may be made especially distinct, when fresh jelly (Fig. F, *a*) *i. e.*, immediately after washing, is occasionally stretched out to from $2–2^1/_2$ times its original length.

In Fig. F, *b* is a rod of jelly after 2 weeks' periodical stretching. This rod broke, on reaching the length of 60 cm. (in Fig. F, *c* is a piece torn off from the rod *b;* the piece is represented a little larger than natural size).

It should be pointed out that it is not always possible to display so successfully the macro-structure which is parallel to the axis of extension, as was done in the experiment illustrated by Fig. F; the rods of jellies resulting from shaking the latex with the LiI solution, when they prove more compact, do not give readily such macro-structures.

The rod of jelly, which was made as compact as possible by mechanical means, does not reveal a macro-structure, and only when strongly stretched does there become distinct the hatching on the surface in a direction parallel to stretching.

Fresh jellies are distinctly vectorial with regard to breaking and to the ability of being elastically drawn out; they may be torn comparatively easily in the direction parallel to their length; whereas in the direction perpendicular to their length, they break only when considerably stretched, *e. g.*, by stretching them 4 times their original length.

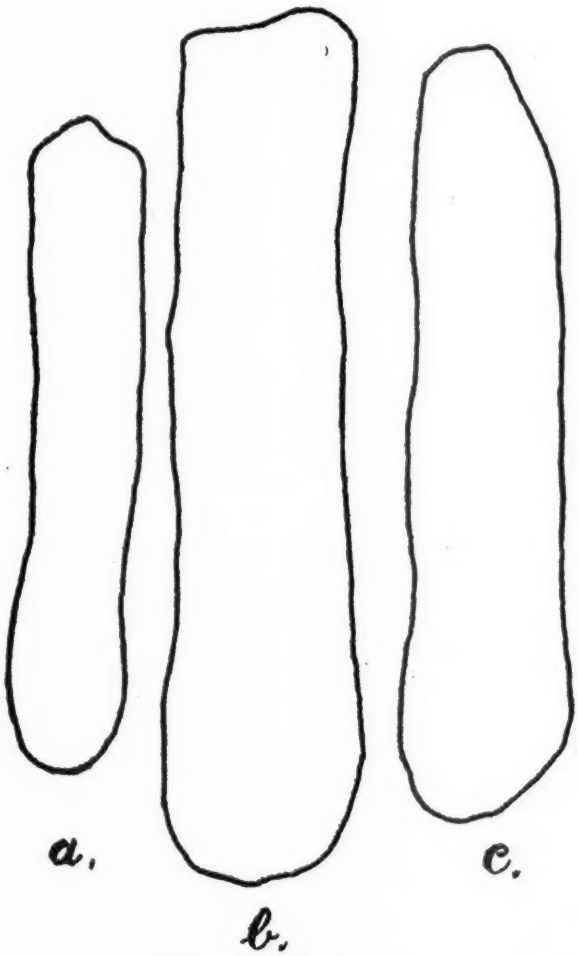

Figure E—Natural Size

Jellies made into plates or balls by mechanical means do not reveal so distinctly vectoriality with regard to breaking and elastical stretching; sometimes they reveal it scarcely at all.

The latex coagula, obtained by pouring latex into boiling aqueous solutions of substances which are dispergators for proteins, have a distinct macroscopical thread-like structure; this structure is very varied and indicates the ropy-plastic stage in the coagulation of latex.

Macroscopical Observations of the Gelatination of Vultex

If the vulcanization of latex be regarded as a process of decreasing the quantity of liquid in the iso-colloidal particles of latex, or as a process of increasing the viscosity of this liquid, or as these two processes working at the same time, then it is possible to foresee the differences between the gelatination of latex and Vultex by the addition to the latter of solutions of substances which are dispergators for proteins.

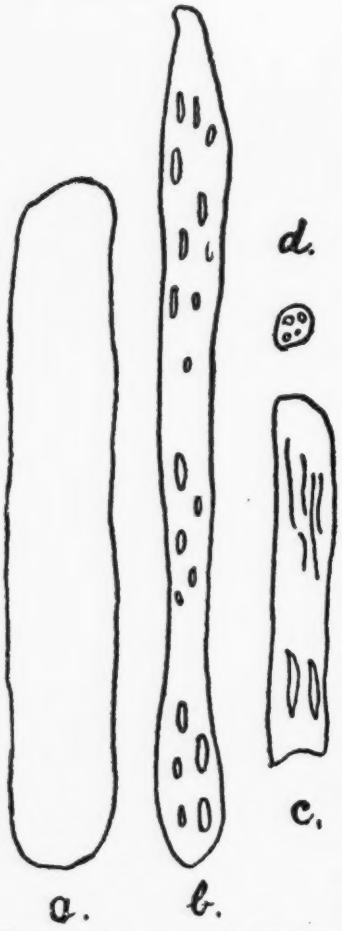

Figure F—(*a*, *b*, and *d*—Natural Size)

Because the flowing together of Vultex particles proceeds more protractedly, they must produce a rod which can be more easily torn to pieces (the rod being obtained by pouring carefully a quantity of Vultex into an equal quantity of aqueous LiI solution, saturated at room temperature; and by shaking this mixture).

The number of particles which have not coagulated in the case of Vultex must be far greater than that in the case of latex.

After the flowing together of the Vultex particles, the stretching out of the rod of jelly obtained requires more effort than the same for a rod of jelly of latex.

All these *a priori* deductions are wholly confirmed by experiments. The experiments were carried out in the same manner as described for latex; only the shaking in the case of Vultex was performed not only once, but three times.

The rod of jelly obtained from Vultex is considerably more porous than that from latex; and, the quantity of the solutions being equal, the Vultex rod is smaller in diameter than the latex one; at the top of the rod of jelly of Vultex there are no sticky films which can be drawn out into elastic threads.

In this case the rod of jelly may be easily taken out of the test tube, leaving behind a non-transparent serum of a greyish white color; the surfaces of the jellies of Vultex are uneven, they have coarse pores and cavities.

The rod of Vultex jelly, which has been washed for three hours in running water, does not stand stretching to twice its length, and becomes broken. When the rod of Vultex jelly is preserved immersed in water, then even after 6 days, it can be easily torn; *e. g.*, a rod of 6.3 cm. length was broken when its length, during stretching reached 9.6 cm. A similar rod of Vultex jelly (6 cm. in length), but taken out of the water and put on filter paper for 24 hours, became more durable and was torn only when reaching the length of 17 cm.

In Fig. G, under *a* is represented the contour of a rod of Vultex jelly after three hours' washing (the uneven places and cavities are not represented; only the contours of the rods are given); under *b* is represented the contour of a jelly after

Plate V

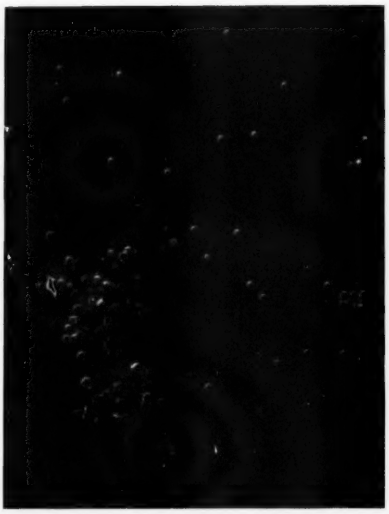

Fig. 27—× 1140

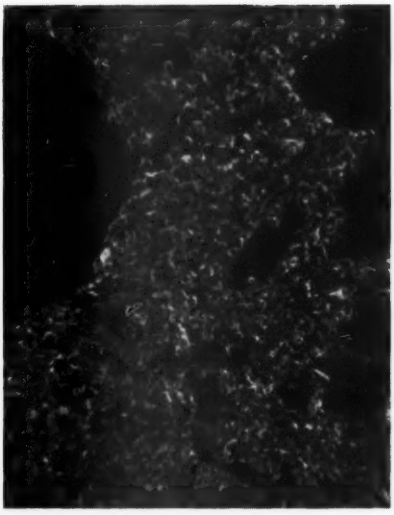

Fig. 28—× 1140

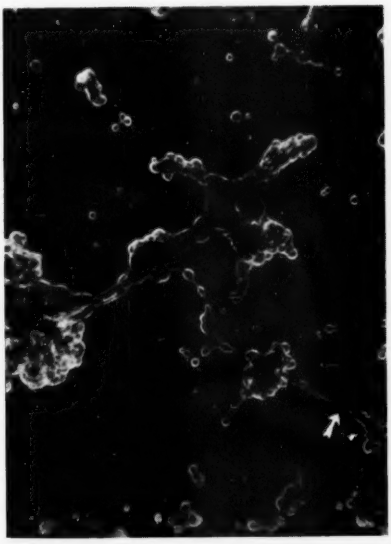

Fig. 29—× 1140

Fig. 30—× 1140

one week's keeping in the room on a pack of filter paper. The rod of jelly *b* may be torn by hand but only by exercising great force.

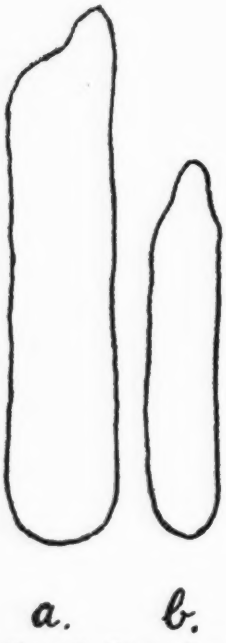

Figure G—Natural Size

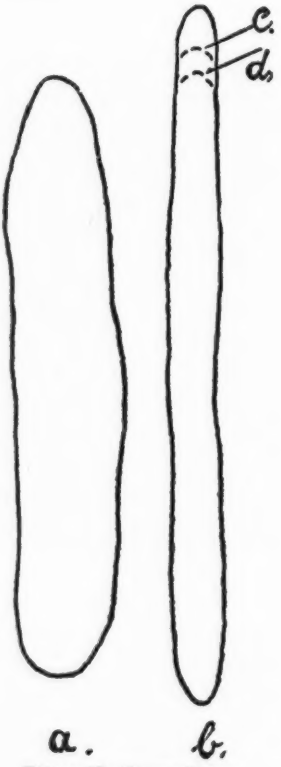

Figure H—Natural Size

Figs. H and I are graphical representations of rods of Vultex jelly quite similar to those of latex, which were illustrated in Figs. D and E. It should be pointed out that no air bubbles, surrounded by elastic films of rubber, were observed during the deformation of Vultex jellies.

In Fig. J, *a* is the contour of a rod of Vultex jelly immediately after washing; *b*—after 2 weeks' drying at room temperature on filter paper. The rod *b* (5.5 cm. in length) was broken up when reaching a length of 36 cm. The stretching of Vultex jelly *b* requires more effort than that of latex jelly (also after drying for two weeks). The jelly of Vultex even after 2 week's drying is of a coarse hollow structure.

The rod of Vultex jelly *b* of 9.5 cm. length, in Fig. H (the shortening of the rod up to line *c* resulted after 5 days' drying, and up to line *d*, after 2 weeks' drying) was torn when reaching the length of about 60 cm. All rods of Vultex jellies show by stretching a more or less distinct thread-like structure, parallel to the direction of stretching.

Thus, although the particles of Vultex flow together much slower than those of latex, they do flow together undoubtedly; and by virtue of the considerably greater cohesive force existing when in course of time there is overcome the greater

viscosity hindering more rapid union, the flowing together of Vultex particles produces systems more resistant to breaking than those obtained by the flowing together of latex particles under equal conditions of experimenting.

In the above mentioned rods of latex and Vultex jellies, even after the lapse of 2 weeks, far from all the particles had flowed together. A complete flowing together does not ensue even after the lapse of several months.

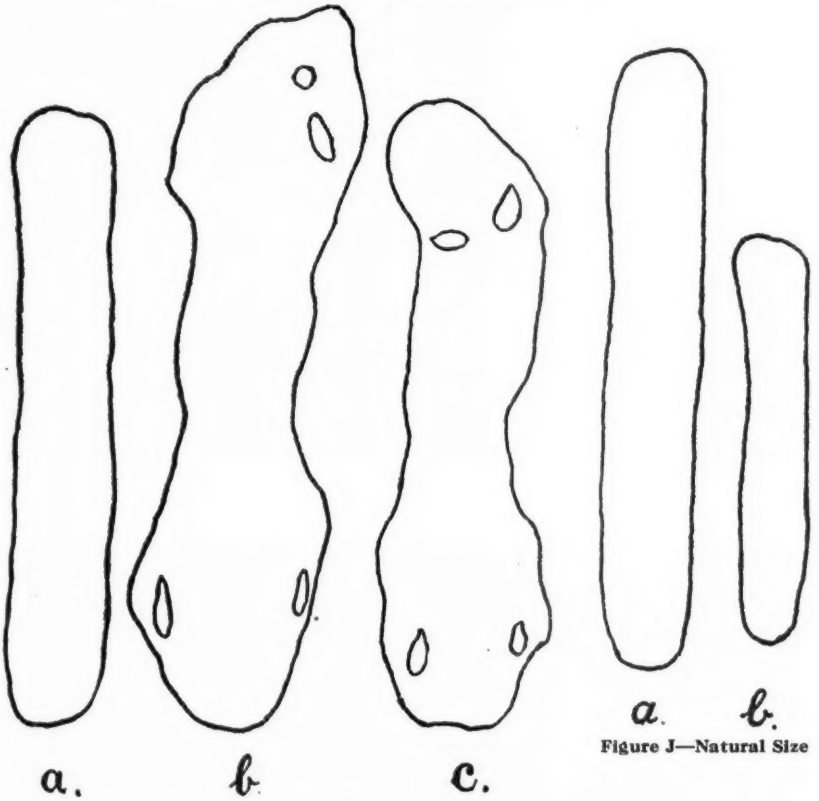

Figure I—Natural Size

Figure J—Natural Size

The mechanical treatment (squeezing, pressing, stretching and the like) of jellies and of other coagula of latex and Vultex accelerates to a considerable extent the process of the flowing together of particles, and shorten considerably the periods of time required for the complete flowing together of all particles.

As I have already stated in another paper,[25] by the evaporation of water from latex as well as from Vultex, there are obtained elastic resistant films; hence in the case of gelatination by drying, there is not observed that difference between latex and Vultex which exists (see above) in the case of the gelatination of latex and Vultex by the addition of substances which are dispergators for proteins.

In the layer of Vultex when it is drying up, the protein-resin envelopes of particles, by drying and syneresis, compress the particles and force the rubber contents of the particles to flow together through the pores and cracks in the envelopes.

[25] P. P. von Weimarn, *Bulletin of the Chemical Society of Japan*, **3**, 157 and following (1928).

Plate VI

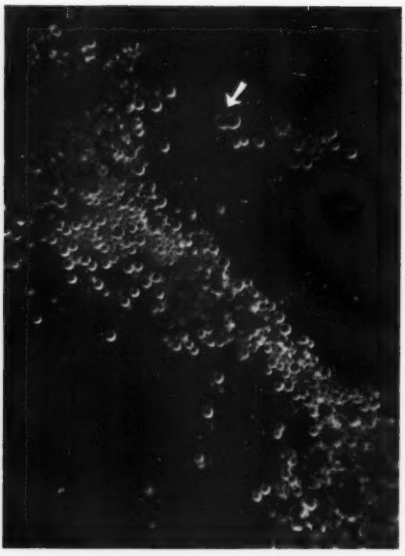

Fig. 31—× 1140

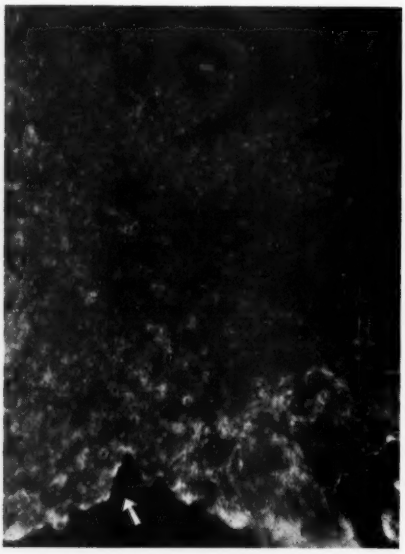

Fig. 32—× 1140

Fig. 33—× 1140

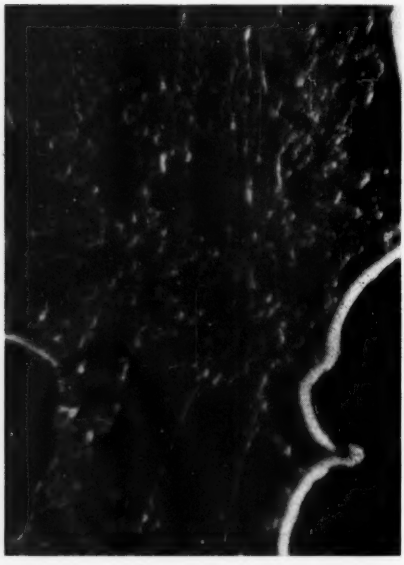

Fig. 34—×1140

Plate VII

Fig. 35—× 1140

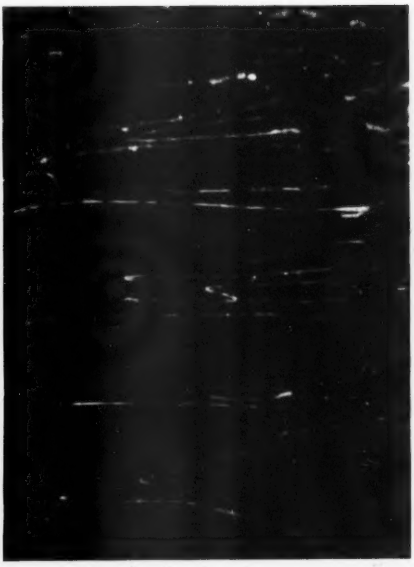

Fig. 36—× 1140

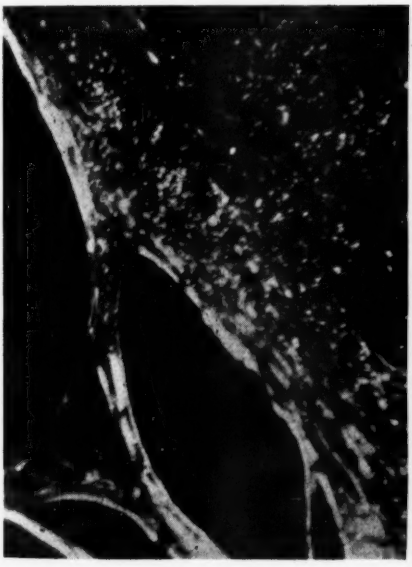

Fig. 37—× 1140

Fig. 38—× 1140

MICRO- AND ULTRAMICROSCOPICAL OBSERVATIONS OF THE GELATINATION (COAGULATION) PROCESSES OF AMMONIA-PRESERVED *HEVEA* LATEX AND *HEVEA* VULTEX

Micro- and Ultramicroscopical Observations of the Processes of Gelatination (Coagulation) of Latex

Five stages of changes in general consistency (and not in the consistency of detached particles) of latex during its coagulation have been described; these stages are easily observed by macroscopical methods.

Of course, all these stages are distinctly observed by micro- and ultramicroscopical investigations.

During the first stage—when the consistency of latex is extremely viscous although the latex is still able to flow slowly—the particles of latex in greater part are not united; and even in the flakes which are not seldom present in the latex in this stage, a quantity of particles are in Brownian movement.

During the paste- or gruel-like stage of consistency (Stage II) the latex consists of flakes and lumps; their structure may be clearly understood from the photo-ultramicrographs of flakes in Fig. 27 (Plate V) and Fig. 31 (Plate VI). On the left side in Fig. 31, a light spot is present; in this part of the flake were assembled many closely distributed small particles of latex, which were still in Brownian movement; the exposition being rather prolonged, these particles have produced the spot on the photographic plate.

During the third stage of consistency, when a part of latex under stretching produces sticky elastic threads, the rubber contents of the adjacent latex particles in certain places have flown together and when such a jelly suffers deformations from outer or inner influences, then threads arise or "connecting links" as they are called by Green; if in addition, these threads suffer pressure from one side, they become flat (*i. e.*, ribbons).

The structure of jelly (coagulum) of latex in the third stage of its consistency is clearly illustrated in the following figures: 28–30 (Plate V), 32 (follow the direction indicated by the white arrow), 34 (Plate VI), 39 (Plate VIII), 52, 53 (Plate XI; in Fig. 51 is represented a film before stretching, and in Fig. 53—a squeezed film; it must be remembered that these pictures were taken by Green using the Zeiss ultra-violet microscope).

When the rubber contents of the adjacent latex particles in a jelly have flown together, then the protein and the other components of the envelopes of these particles will naturally arrange themselves within these flown together rubber contents.

In Stage II of gelatination (let us assume that the gelatination is caused by the evaporation of water from latex) we have an example of a micro- and ultramicro-cellular (membranous) jelly;[26] the walls of the cells are plastic-solid membranes composed chiefly of non-rubber parts of serum, and the content of cells is rubber. In pores (between the adjacent particles) and in the cavities of jelly is serum.[27]

In Stage IV we have a rubber disperse medium (its structure will be discussed later) in which as a disperse phase are distributed the particles (pieces of envelopes of latex particles) of the non-rubber components of latex.

It is a difficult matter to make a preparation for microscopical investigation,

[26] P. P. von Weimarn, *Reports of the Imperial Industrial Research Institute of Osaka*, **9**, No. 3 (June, 1928).

[27] It has been already shown by the investigations of Philip Schidrowitz (*Kolloid-Z.*, **4**, 87–88, 1909) that the films of rubber consist of adjacent particles of latex; however, such structure is appropriate only to the initial stages of the gelatination of rubber.

Plate VIII

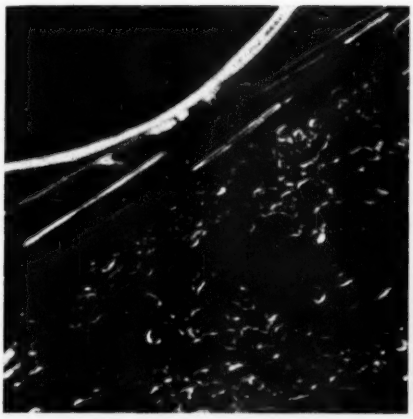

Fig. 39—× 1140

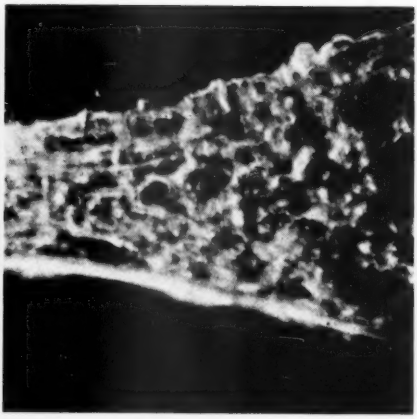

Fig. 40—× 1140

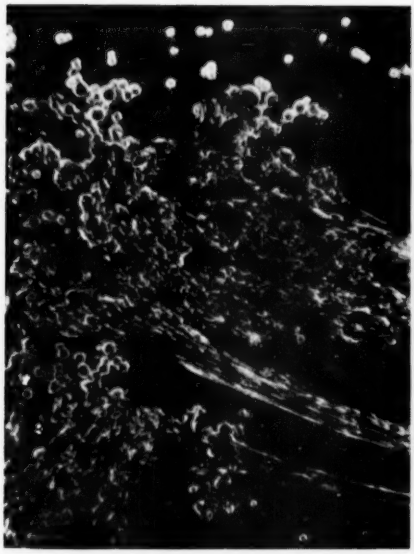

Fig. 41—× 1140

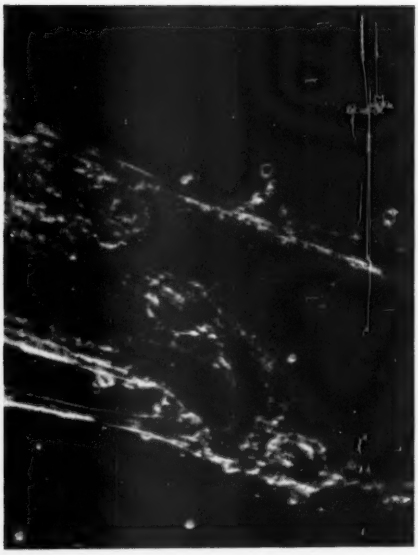

Fig. 42—× 1140

in which were fixed only one stage of gelatination; usually we have in the preparation several stages of gelatination.

However, Figs. 35–38 (Plate VII) convey a clear idea of the structure of coagula. Of most interest are Figs. 35 and 36, from which it is clearly observed how the ropy-plastic (Fig. 35) consistency of the rubber mass passes into a more elastic one (Fig. 36).

In Figs. 37 and 38 are represented preparations (jelly-films obtained by drying up latex) which have partially passed into Stage V of gelatination; the rubber mass in certain places of these preparations has a fibril structure resulting from strains in the films.

It is of interest to point out one transition state of the jelly (coagulum) of latex. When a film of latex in Stage III of gelatination—*i. e.*, in that stage when the latex particles have connected themselves in certain points by their rubber contents—is carefully drawn out, the film will disintegrate into a range of threads closely distributed parallel to each other; if then the film is stretched in a direction perpendicular to the former stretching, the threads will separate from each other, giving characteristic "fluidal" structures, one of which is represented in Fig. 33 (Plate VI). Such threads, or shorter ones, may be easily rolled up by means of a sliding movement of the cover-glass, into long worm-like rollers (Fig. 57, Plate XI. Compare the experiments of Beadle and Stevens).

Stage V is a highly elastic stage of the gelatination of latex; this stage is illustrated by, *e. g.*, Figs. 37 and 38 (Plate VII), Fig. 40 (Plate VIII), Fig. 46 (Plate IX) and Fig. 55 (Plate XI).

The change in consistency of the rubber contents of latex particles—like the change in the consistency of fibroin (natural silk) caused by the weaving of silk by silk-worms—must be ranked among the most typical cases of "coagulation or solidifying produced by movement" or as a "coagulation or solidifying produced by stretching;" as it is evident that stretching is only a particular case of the setting in motion of a viscous or ropy-plastic mass, the term "coagulation or change of consistency by movement" will suit best this phenomenon.

Whether the gelatination results from the evaporation of water from latex, or from the addition of latex to the concentrated aqueous solutions of substance-dispergators for proteins (*e. g.*, LiI aqueous solution), in both cases during the syneresis and drying up of the initially soft and partially sticky paste-jelly, the particles of latex undergo deformation and contraction, and owing to these "inner" mechanical actions, the rubber contents of latex particles do not remain quiet, but move; and by this movement the consistency of the rubber contents of particles is changed. The "outer" mechanical action (stretching, pressing) accelerates the process of the "change of consistency of rubber by movement." From these movements results the fibril structure of rubber (see, *e. g.*, Figs. 37 and 38 in Plate VII, Fig. 40, Plate VIII, Fig. 55, Plate XI).

In Figs. 41 and 42 (Plate VIII) is represented a micro-flake of latex; this flake is drawn out under pressure (screw-press); in Fig. 41 is seen one-half of this drawn out flake, in Fig. 42—the second half of the same micro-flake. (Compare Fig. 58, Plate XI and Fig. 60, Plate XII; by stretching the coagulum of rubber, in this preparation are obtained threads of vanishingly small thickness.)

In Figs. 43–46 (Plate IX) are represented four stages in a progressive stretching of a jelly film, obtained by evaporation of latex. In the last stage (Fig. 46) when the film is being stretched in a direction perpendicular to the original direction of stretching, it becomes easily separated into fibres, the latter into fibrils, *i. e.*, the rubber begins to display distinct "fibril cleavage."

In Fig. 46 (look in the direction of the white arrow) is clearly seen a shell of latex

Plate IX

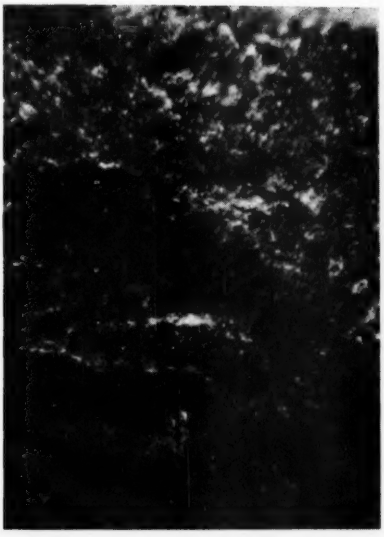

Fig. 43—× 1140

Fig. 44—× 1140

Fig. 45—× 1140

Fig. 46—× 1140

particles, which is completely or only partially freed from the inner rubber contents.

Micro- and Ultramicroscopical Observations of the Gelatination (Coagulation) Processes of Vultex

Since the only essential difference between the process of gelatination of Vultex and that of latex lies in the fact that the process of flowing together of the rubber contents of particles is slower in the case of Vultex, it is sufficient for the illustration of the process of gelatination of Vultex, to present four photoultramicrographs taken of the films of Vultex jelly; the films were obtained by drying the Vultex. These photoultramicrographs produce evidence to the effect that the rubber contents of Vultex particles flow together and that the rubber acquires "fibril structure" and "fibril cleavage;" see Plate X, Figs. 47–50.

By exerting pressure upon the cover-glass covering Vultex (1:200) mixed with a concentrated aqueous solution of lithium iodide, no ropy-plastic stripes are produced as is the case with latex (Figs. 29 and 30, Plate V); when the aggregates of Vultex particles in a LiI solution are pressed stronger, then the distinct net of contours produced by the adjacent particles of Vultex become indistinct.

A strong pressure upon the preparation of Vultex with a screw-press gives results similar to those in the experiments with latex (see Plate IV).

The Multiplicity of Structure Possessed by Jellies and by Other Coagula of Latex and Vultex

Not only do the time of existence and aging influence the changes in the structure of jellies of latex and Vultex, but even in the same piece (*e. g.*, in a rod of jelly obtained by shaking latex or Vultex with a LiI solution) of latex or Vultex jelly, there are present structures different in the various sections of the piece, *i. e.*, here we have a mosaic of structures.

Fresh, or it would be better to say, young jellies of latex or Vultex, according to my classification must be ranked with poly-disperse micro- and ultramicrocellular (membranous) jellies; whether we produce the gelatination merely by evaporating the water from latex, or pour the latex into a concentrated aqueous solution of LiI, the composition of the membranes of cells will be evidently different.

Old jellies of latex or Vultex, which were as uniformly as possible treated mechanically, must be ranked with jellies possessing inner fibril structure, or, it would be better to say, to jellies with fibril cleavage. The degree of dispersity (the length and thickness) of the fibres which are in such jellies, as is evident, is dependent upon the life history of this jelly. There may be present here a coarsely disperse fibrous structure—if the heterogeneity owing to the presence of the non-rubber components of jelly be not taken into account—a completely latent fibril cleavage may be present, *i. e.*, a micro- and ultramicroscopically homogeneous system.

A jelly of rubber may also possess a lamellar structure, *i. e.*, it may consist of layers of lamellae, each of which is built up of parallel fibrils; the fibrils being arranged parallelly to each other in every lamella may of course be distributed in different lamellae at different angles to the fibrils of adjacent lamellae.

A clear understanding of the whole variety existing in the structure of jellies and of other coagula of rubber may be derived only from the clear understanding of the causes underlying the rubber-like state.

In the preface to this paper I have already exposed these causes, as I understand them; now I wish to outline again briefly these causes, treating rubber not only as a mixture of liquid and solid isomers, but also as a chemical individual pos-

Plate X

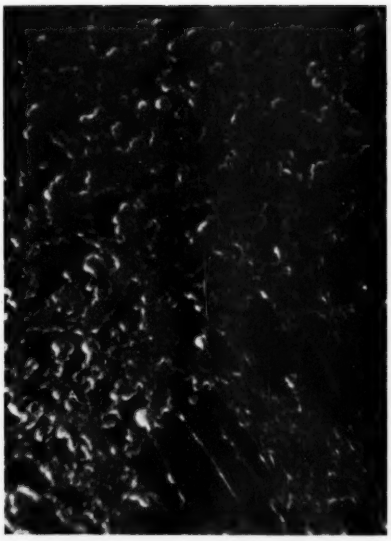

Fig. 47—× 1140

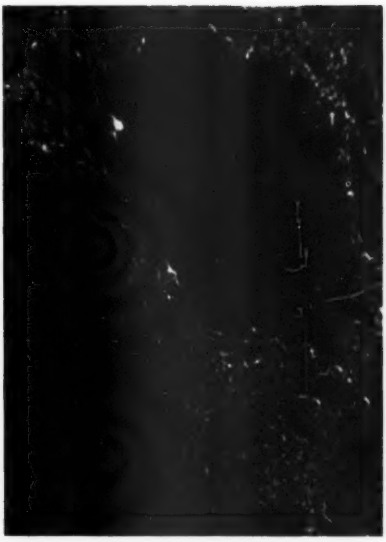

Fig. 48—× 1140

Fig. 49—× 1140

Fig. 50—× 1140

sessing, in addition to the usual melting point, another special temperature, the temperature of the dispergation of rubber into mono-dimensional vectorially constructed aggregates of molecules.

Rubber as a System Composed of Two Isomers

Worthy of note here is the scientific courage shown by Hauser when he frankly renounced[28] the hypothesis of Freundlich and Hauser which attempted to explain many changes in the properties of rubber by the two-phase structure of separate particles of latex.

Of course, the cause of high elastic properties of rubber lies only[29] in the inner rubber contents of latex particles.

My views,[30] expressed briefly in the preface to this paper, are concerned only with the rubber contents.

In order to explain the long existence of high elastic properties of rubber, when considering rubber as a mixture of liquid and solid polymers, the assumption must be made that a liquid polymer is being extremely slowly transformed into a solid one.

And when the fact is taken into account that rubber may be drawn out into threads of such an extreme fineness that even under the most contrasted ultramicroscopic illumination of the preparation (look at Figs. 29, Plate V, 56 and 58, Plate XI, 59 and 60, and Plate XII, following the indication by the white arrow) and with the highest aperture possible of the objective, these threads are only just visible, or their middle (the finest) parts are even absolutely invisible,[31] then the rubber molecules themselves must be endowed with spiral structure.

Only by making these two assumptions may be understood without any difficulty all the data of the micro- and ultramicroscopical study and, in general, all the experimental results.

Rubber as a Chemical Individual Possessing a Temperature of Dispergation into Mono-dimensional Vectorially Constructed Aggregates of Molecules

If, for clearness sake, we imagine the distribution of intensities in the vectorial field of a molecule of a substance with one usual melting point to be in the form of an ellipsoid not very greatly differing from a sphere, then we shall be able to understand easily that, when reaching the melting point, a crystal disintegrates into separate molecules.

Now if we imagine the distribution of intensities in the vectorial field of the molecule of a certain special substance as an ellipsoid flattened to the form of a thin plate, then it will be easily understood that at a certain temperature, lower than the usual melting point, there will ensue a disintegration of the crystal of the substance under discussion, into lamellae, *i. e.*, this substance will possess one more special temperature, which may be called "the temperature of the dispergation of substance into two-dimensional vectorially constructed aggregates of molecules."

Finally, if the molecule of a certain other special substance possesses a vectorial

[28] E. A. Hauser, "Latex," p. 164, Dresden, 1927. Unfortunately in many papers appearing on rubber this incorrect hypothesis is being continually returned to.

[29] The rôle of proteins, resins and of other non-rubber components of latex is analogous to the rôle of the so-called "active filling material (active Füllstoffe)" used in the bettering of the mechanical properties of rubber.

[30] These views appeared in a publication for the first time in *Reports of the Imperial Industrial Research Institute of Osaka*, **8**, No. 13, 75–80 (November, 1927).

[31] After the lapse of some time, if the stretching be continued further, the thread breaks up in this middle part; the broken ends become somewhat thicker and curled spirally into a small lump (see Fig. 59).

Plate XI

Fig. 51

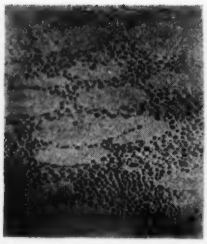

Fig. 52 (After Henry Green)

Fig. 53

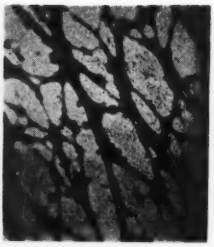

Fig. 54

Fig. 55—× 1140

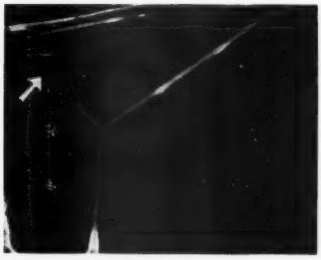

Fig. 56—× 1140

Fig. 57—× 1140

Fig. 58—× 1140

field, the distribution of the intensities of which may be represented in the form of a thin ellipsoid drawn out like a needle with ellipsoidal ends, then before reaching the usual melting temperature, the crystal of the substance under discussion will disintegrate into fibrils; this temperature may be called "the temperature of the dispergation of substance into mono-dimensional vectorially constructed aggregates of molecules."

Let us suppose that rubber is just the substance possessing a special temperature designated by me as the temperature of the mono-dimensional dispergation of substances.

This temperature, lying for rubber probably somewhere not very far from 0° will be its apparent temperature of fusion (or solidifying), whereas its true melting temperature (*i. e.*, the temperature of the disintegration of the fibrils into molecules) will be somewhere near 200° C.

It is clear that a substance composed of molecules possessing the above-described distribution of intensities in its vectorial fields, will easily change its consistency under the influence of mechanical actions; because the breaking of fibrils into smaller ones is tantamount to an approaching to the liquid state; on the contrary, every movement, *e. g.*, by means of stretching the substance, of short fibrils in a direction parallel to each other, gives them more chance to unite into longer fibrils by way of a mutual union by the regions of the vectorial fields with highest intensities.

The rubber is usually applied and treated at the temperatures lying below the temperatures corresponding to the destruction of the connection for the regions of high intensities of vectorial fields of its molecules (it is the melting temperature for these regions) and above the temperature of the disturbance of the connection for other regions of the same vectorial fields (this is the melting temperature for these regions).

"Heat inhomogeneity" as understood in the sense of Clerk Maxwell, for the substances possessing such extremely unequal distribution of intensities in vectorial molecular fields, plays a special rôle in the sense of influencing the general consistency of the system: the molecules which are hotter (the temperature measured by the thermometer is constant) give the liquid part, those colder work as factors for the union of the fibrils of mono-molecular thickness into thicker fibres.

Systems possessing molecules of the character discussed above, with ease (completely or only in certain places of the system) keep overcooled conditions, and these conditions may be changed by mechanical influences of different character.

With the above view it is not difficult to comprehend that rubber can be considered also as a substance which under ordinary temperatures is in an aggregate-fluid crystalline state.[32]

In future parts of this work of mine, in connection with the experimental matter given in them, I shall have many opportunities of comparing these views, those exposed in paragraph 1, and in paragraph 2, and of deciding which of them throws most light upon the facts.

My basic conception of the cause of the rubber-like state of matter is in accord with both these views.

[32] von Weimarn, *Bulletin of the Chemical Society of Japan*, **3**, 157 (1928).

Plate XII

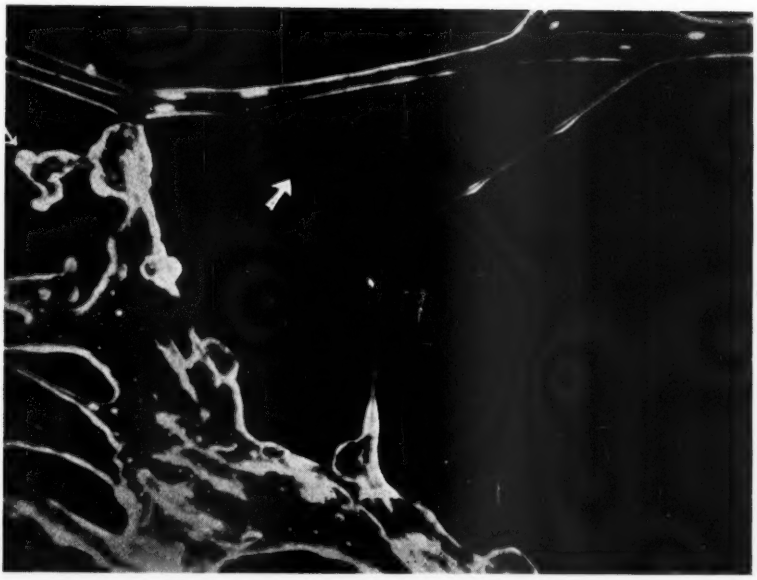

Fig. 59—
× 2375

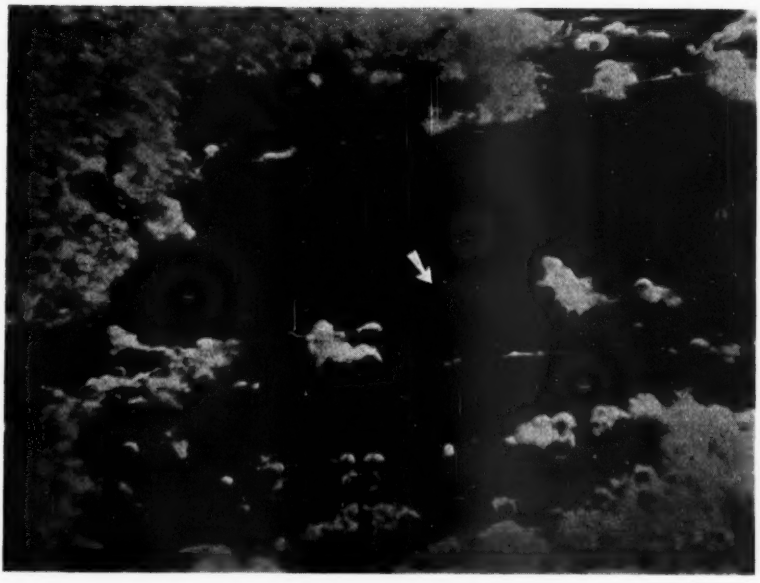

Fig. 60—
× 2375

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The Vulcanization of Rubber

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Although vulcanized rubber articles have been in common use for more than three-quarters of a century, nevertheless the mechanism of the vulcanization process has never been satisfactorily explained. The rubber industry has recently grown to tremendous proportions. The introduction of organic accelerators has improved the physical properties of the rubber vulcanizate to such an extent that it has made possible the production of the modern automobile tire.

All the progress that the industry has made in improving the vulcanization process has been brought about by empirical means. The "Edisonian" type of research that enabled Charles Goodyear to discover vulcanization is, even to this day, the system that is primarily employed in the rubber industry. Outside the classical work of C. O. Weber[1] very few attempts have been made to study the subject of vulcanization from a systematic and scientific point of view. In studying the theories of vulcanization propounded by various investigators as outlined in a series of articles by Dubosc,[2] one immediately notices that the work of these investigators lacks coherence. Most of them draw sweeping generalizations from a small amount of experimental data confined to a narrow branch of the vulcanization problem, at the same time ignoring work performed in other fields of the same subject. Some of them seem to dodge the main issue of the problem. André Dubosc[3] goes into elaborate detail in describing the formation of an active form of sulfur during the vulcanization process, but does not seem to be very much interested in what follows.

Things were in a rather chaotic condition until the advent of Wolfgang Ostwald[4] in 1910. After surveying the results of the various investigators, and being an orthodox colloid chemist, he came to the conclusion that the available data was more in accord with a process of adsorption of sulfur by rubber than one in which sulfur entered into chemical combination. Ostwald's stand produced a beneficial effect in that it encouraged discussion and proved an incentive to further research on the subject of vulcanization. It helped rubber chemists to orient themselves so that the work undertaken was not done blindly. The issues of the subject were becoming plainly defined. Either chemical combination took place during the process, or it was simply a case of adsorption. From this one could deduce the possibility that it may be a combination of both.

Before discussing any of the existing theories of vulcanization, it would be advisable to define some of the terms connected with vulcanization. When a rubber-sulfur mixture is subjected to a temperature of about 120–150° C. for some time, one notices a gradual change in the physical properties of the product. The temperature limits are not well defined and are changed radically by the presence of various accelerators. The lower the temperature the longer it takes the product to attain the desired changes in physical properties. The original object of vulcanization was to decrease the effect of temperature changes on the rubber, since

[1] "The Chemistry of India-Rubber," 91 (1902).

[2] *Rubber Age* (*N. Y.*), **16**, June–December (1924).

[3] *Rubber Age* (*N. Y.*), **16**, 120 (1924).

[4] *Kolloid-Z.*, **6**, 136 (1910).

the raw rubber becomes sticky when hot. Apart from this, there are other very noticeable temperature changes. If a piece of unvulcanized rubber is stretched and then chilled in ice water, it remains stretched. A piece of vulcanized rubber, for example an ordinary rubber band, snaps back after receiving the same treatment. A piece of partially vulcanized rubber, particularly if vulcanized with ultra-accelerators, may appear to have at room temperature about the same properties as the well-cured rubber band; but it will retract very slowly in ice water after being stretched. Both the partially vulcanized and the unvulcanized rubbers resume their original shape, or very nearly so, when they are brought back to room temperature.

On vulcanization, the raw rubber mixture undergoes other decided changes, becoming more resistant to solvents, stretching, abrasion, and the action of chemical agents, and also increasing in strength. These desirable changes in physical properties may be brought about also by the use of other agents. When raw rubber is treated with a dilute solution of sulfur chloride, it is not necessary to heat the product in order to attain the desirable physical properties characteristic of a vulcanized product. Raw rubber has been successfully vulcanized with *m*-dinitrobenzene,[5] trinitrobenzene, and with similar compounds; but these products proved to be of academic interest only, and never were able to assume the commercial importance allotted to the two classical methods mentioned above. The term vulcanization as commonly used in the rubber industry, is really confined to the process that causes a change in the physical properties of a raw rubber mixture which makes the product useful commercially. Vulcanization may, therefore, be defined for practical purposes as the change in physical properties due to the action of sulfur, or sulfur monochloride on rubber. A complete theory of vulcanization must, of course, include the somewhat similar changes in properties produced by oxygen, selenium, etc.; but it is simpler and wiser to consider the sulfur vulcanization first and later to see how far the conclusions are applicable generally.

The word "cure" is very often used synonymously with the term vulcanization, but really designates a particular stage in the process of vulcanization that yields a product of commercial value. If a product has acquired the desired physical properties, it is said to be "properly cured." If it has not reached that stage, it is said to be "undercured," and when it is heated too long, it is said to be "overcured." During the process of vulcanization some of the sulfur becomes firmly attached to the rubber, whereas the remainder can be extracted easily by suitable solvents. The sulfur held in firm combination is called "combined sulfur," and the percentage of combined sulfur present, based on the original amount of raw rubber, is called "coefficient of vulcanization." One must bear in mind that the amount of combined sulfur present is not a measure of the degree of vulcanization. The attainment of the physical properties characteristic of a properly cured rubber mixture depends to a great extent on the presence of foreign ingredients such as accelerators. By the use of some organic accelerators it is possible to produce a vulcanized sample containing much less than 0.5 per cent of combined sulfur. Some of the physical properties of this sample may be far superior to those of any properly cured sample, not containing any accelerator and having a combined sulfur content of over 3 per cent. It is, of course, possible that a large part of this variation in properties may be due to the milder heating conditions.

The use of accelerators in the vulcanization of rubber is a very important phase of the rubber industry. They perform two functions:

In the first place, they reduce the amount of heat necessary for the process of

[5] Stevens, *J. Soc. Chem. Ind.*, **36**, 107 (1917).

vulcanization. Some of them are quite effective at temperatures much lower than those formerly used.

In the second place, their use improves the quality of the product obtained. The chief aim in the early development of the industry was to use accelerators for the purpose of shortening the time of cure. At present, accelerators are selected also on the basis of added physical properties.

Now that we understand what is meant by vulcanization we can proceed to discuss some of the theories that have been propounded to account for the peculiar phenomenon. Weber[6] was the first to formulate a theory that was substantiated by adequate scientific experimental data. The fact that portion of the sulfur was taken up by the rubber in such a way as to be no longer extractable by solvents for sulfur, was regarded as evidence that chemical combination had taken place. Since the reaction was not accompanied by the evolution of hydrogen sulfide. Payen[7] had suggested that the process was one of addition and not substitution. The limit of combination of rubber with sulfur was shown to be reached in the formation of a compound having the empirical formula $C_{10}H_{16}S_2$ (polyprene disulfide). Weber regarded this as the highest member of a series of polyprene sulfides the lowest member of which was a compound represented by the formula $(C_{10}H_{16})_{10}S$ containing 2.29% sulfur. This was assumed to be the lowest compound because the properties of vulcanization first became apparent when the combined sulfur was present to the extent of 2 to 2.5%. Weber assumed that it was impossible to obtain any evidence of the formation of separate members of this series of compounds, since the alteration in properties from unvulcanized to vulcanized soft rubber and then to hard rubber was a gradual one, characterized by no sudden changes in any of its properties at any stage in the process.

While Weber's experiments indicated that the progress of vulcanization was accompanied by a chemical reaction, his explanation did not seem entirely adequate, since it was possible, by use of accelerators, to vulcanize rubber with a smaller amount of sulfur than he had postulated for his smallest molecule $(C_{10}H_{16})_{10}S$. Weber's explanation accounts for the facts better than any other theory, but the main objection to it is that it is almost impossible to check it experimentally. By definition, it is assumed that the various members of the series of compounds formed are so closely related to each other in properties that it is naturally impossible to separate them.

A great many theories followed Weber's, but these may be regarded as the forerunners of the adsorption theory that was propounded by Wolfgang Ostwald in 1910. After considering all the results of previous workers, Wolfgang Ostwald sought to show that the available data was more in accord with a process of adsorption of sulfur by rubber than with one in which sulfur entered into chemical combination with the rubber. A very good discussion of the adsorption theory is found in Luff's book,[8] from which a good many of the facts have been taken.

The chief facts on which his hypothesis was based were as follows:

(1) In all vulcanized rubber there is present free sulfur which would not be expected if a chemical reaction were involved.

(2) According to Höhn,[9] vulcanized rubber on sufficiently prolonged extraction could be freed entirely from sulfur.

(3) The rubber always takes up sulfur in a purely additive manner.

(4) A continuous series of addition products is formed, the first and last members of which have no definite stoichiometrical composition.

[6] "The Chemistry of India-Rubber," 91 (1902).

[7] *Compt. rend.*, **34**, 2 (1852).

[8] "The Chemistry of Rubber," 95 (1924).

[9] *Gummi-Ztg.*, **14**, 17, 33 (1899).

(5) The amount of sulfur adsorbed by the rubber increases with the previous mechanical treatment. This could be explained by assuming rubber to consist of a two-phase system, the degree of dispersion of the disperse phase and hence the adsorptive capacity, being thus increased.

(6) The capacity for taking up sulfur increases with rise in temperature and the temperature coefficient is more nearly in accord with an adsorption process.

(7) The fixation of sulfur at a given temperature does not take place uniformly, as the breaks in Weber's curve show; this phenomenon is frequently met with in the adsorption of water by certain gels, for example silicic acid.

(8) Adsorption proceeds in accordance with the exponential equation $x/m = kc^n$, where x is the weight of the adsorbed substance, m is the weight of the adsorbent, and k and n are constants.

The views put forward by Wolfgang Ostwald created a great deal of excitement and at the same time were a cause for further research which immediately established the inaccuracy of most of the facts upon which the adsorption theory was based.

With reference to the assumption that free sulfur is always present in vulcanized rubber, this is quite true with regard to the rubber heated with sulfur for a sufficient time to permit the characteristics of vulcanization to be assumed. It was shown, however, by Spence and Young[10] that on heating a mixture of 100 parts rubber, first extracted with acetone to remove resins, with 10 parts of sulfur for 30 hours at 135° C. and 10 hours at 155° C., respectively, no sulfur could be extracted on treatment with acetone.

Höhn's statements that all the sulfur could be extracted from vulcanized rubber failed to be verified by other workers. Stevens[11] cured a rubber mixture containing 10 per cent sulfur for 30 minutes at 145° C., and after 9 weeks' extraction with acetone, the sample still contained 1.55% sulfur. Other samples were treated in similar manner, but in all cases sulfur remained in the extracted sample even after 9 weeks' extraction.

In reference to the additive nature of the process, nobody ever questioned it after Weber's experiments showed the absence of hydrogen sulfide from the products of the reaction. The statements that none of the compounds formed by rubber-sulfur combination contained sulfur in stoichiometrical proportion was not in agreement with Weber's experiments, which showed that the highest limit of combination corresponded closely with the compound $C_{10}H_{16}S_2$. Spence and Young corroborated Weber's results by vulcanizing a rubber-sulfur mixture containing 63 parts rubber and 37 parts sulfur at 135° C. for periods varying from 1 to 30 hours. At the end of 18.5, 20, 25, and 30 hours the proportion of sulfur left in the residue after extraction of free sulfur was 31.75, 31.97, 31.91, 31.97, respectively. The samples after 20 hours' vulcanization still contained about 4% free sulfur, so that the stopping of the reaction was not due to lack of sulfur.

The formation of an upper limit compound was further emphasized by Hinrichsen and Kindscher,[12] who heated rubber in cumene at 170° C. with proportions of sulfur increasing to 400%, calculated on the rubber present. In all cases a dark brown substance was obtained containing not more than 32% of combined sulfur.

With regard to the statement that mechanical working affected the rate of combination with sulfur, Weber[13] had previously enunciated as a general principle that rubber containing a certain proportion of sulfur gave the same chemical

[10] *Kolloid-Z.*, **11**, 28 (1912).
[11] *J. Soc. Chem. Ind.*, **38**, 195T (1919).
[12] *Kolloid-Z.*, **11**, 191 (1912).
[13] "The Chemistry of Rubber," 94 (1902).

result on vulcanization for a given time whether it had previously been subjected to mastication for a prolonged or normal period, although the physical properties might be widely different. Spence and Ward[14] were able to corroborate these results. They found that the rate of combination of rubber with sulfur was the same whatever the mechanical treatment; but, in order to obtain products of equal tensile strength, it was necessary to vulcanize for a longer period in case of the overmilled sample than in the case of the normally milled sample, and thus a higher coefficient of vulcanization was obtained.

According to Weber's results, the rate of fixation of sulfur at a given temperature was not uniform, and thus the breaks in the curve were held to support the adsorption theory. Of course, Weber himself suggested that the breaks in the curve might be interpreted as due to the formation of various chemical compounds, but finally decided that they had no such significance, since these irregularities appeared at different places when vulcanization was carried out at different temperatures. He, therefore, concluded that they probably indicated a particular physical, rather than some definite chemical condition of the vulcanization product. Spence and Young repeated Weber's experiments, at the same time trying to eliminate all sources of error. They worked with acetone-extracted rubber so as to prevent the lack of uniformity that might result from the reaction of sulfur with non-rubber substances proceeding at a different rate from that of the rubber portion. Special care was also taken in reference to controlling the time of heating; and, in general, the technic governing the entire experiment was a vast improvement upon that of Weber. Samples of a mixing of 90 parts rubber and 10 parts sulfur were heated at 135° C., and various test samples were taken out at intervals. The combined sulfur was determined and the results obtained plotted against time of heating gave a smooth curve. A similar set of experiments was carried out at 155° C., the results of which, likewise, produced a smooth curve when plotted.

The velocity coefficient k of the reaction was calculated from the equation $k = x/t$, where x is the percentage of sulfur entering into combination in time t. The temperature coefficient of the reaction velocity calculated from van't Hoff's equation was found to be 2.65 for 10 degrees increase in temperature, a value agreeing with those generally obtained in case of a chemical reaction. Some experiments were performed at temperatures below 100° C., and from this series the temperature coefficient was calculated to be 2.84, which is within the limits characteristic of a chemical compound.

Further evidence in favor of a chemical combination is afforded by the experiments of Spence and Scott.[15] They found that when bromine reacts with vulcanized rubber, instead of combining in the ratio of 4 atoms of bromine for every $C_{10}H_{16}$, the resulting compound contains less bromine than required to form the tetrabromide, the balance being made up of the equivalent of sulfur.

Venable and Green[16] have shown that sulfur is quite soluble in rubber. This would naturally preclude the possibility of an adsorption complex between the sulfur and the rubber unless one made the unwarranted assumption that the sulphur suddenly crystallized out from solution and then became adsorbed on the rubber. This discussion of the theory of pure adsorption has brought forward an overwhelming amount of evidence in favor of the occurrence of a chemical reaction during the process of vulcanization.

The controversy regarding the validity of the two classical theories naturally

[14] *Kolloid-Z.*, **11**, 274 (1912).
[15] *Kolloid-Z.*, **8**, 304 (1911).
[16] *J. Ind. Eng. Chem.*, **14**, 319 (1922).

led to the formulation of theories that were to some extent a combination of both the chemical theory and the adsorption theory. Ostromuislenskii[17] considers vulcanization as a process in which only a small proportion of the rubber enters into combination with sulfur to form a compound in which the unchanged rubber is swollen or adsorbed. The reverse condition may equally hold in which the compound formed is adsorbed by the unchanged rubber.

Axelrod[18] has assumed a process of polymerization in order to account for the change in physical properties. He claims that vulcanization is a process in which there occurs a simultaneous "depolymerization" by means of heat and a "polymerization" due to the sulfur with simultaneous formation of a sulfur addition product. It is not clear just what the author means by the term "polymerization." The term may refer to the chemical process of polymerization or it may be regarded as the reverse of the effect noted when rubber is submitted to mechanical working.

An explanation postulating a process of chemical polymerization or physical aggregation, or a combination of the two, is not a foolish one, since we may regard rubber itself as a polymerization product of isoprene. This transformation has changed a liquid, soluble in many organic solvents, into an elastic substance which is insoluble in many liquids capable of dissolving the parent hydrocarbon. It is, therefore, possible that rubber itself may be further polymerized to form a product that is still more resistant to solvents, and with more marked elastic properties. So far all the agents that have been known to induce this polymerization (vulcanization) have at the same time entered into some sort of a chemical combination. Another objection to this theory is the fact that once the polymerization has been brought about, it is impossible to reverse the process by depolymerizing the vulcanizate chemically so as to yield the original raw rubber.

Kirchhof[19] has put forward a modification of the above theory in which he assumes vulcanization to be a transformation of the rubber from an unstable to a relatively stable form, the chemical combination of sulfur being regarded as a subsidiary process.

Of course, there are many more theories on the subject of vulcanization than those outlined above. Many of them are simply modifications of various phases of the above theories; some of them dodge the subject of vulcanization by expending their energies in accounting for an active form of sulfur, while others are of no use as working hypotheses since they are based on assumptions that would be almost impossible to submit to experimental verification.

Before investigating the subject of vulcanization any further, one should remember some of the well-established facts regarding the process of vulcanization that must be explained by any workable theory.

In the first place, most people will agree that rubber will combine with sulfur in the presence of an excess of the latter to form a definite chemical compound whose empirical formula is $(C_5H_8S)_n$.

When approximately 0.5% sulfur is mixed with raw rubber and the mixture subjected to the heating process of vulcanization, a tacky (sticky) mass is obtained that is similar to raw rubber subjected to the same heating process. All the sulfur may be held in firm combination by the rubber, but nevertheless the physical properties of the product are practically identical with those of the original raw rubber. No matter how long we may heat this product, it appears to be undervulcanized and resembles the raw rubber. As we increase the percentage of sul-

[17] Luff, "The Chemistry of Rubber," 103 (1924).
[18] *Gummi-Ztg.*, **24**, 352 (1909).
[19] *Kolloid-Z.*, **13**, 49 (1913); **14**, 35 (1914); **26**, 168 (1920).

fur in the vulcanizate, the physical properties undergo change gradually. The change is a gradual, continuous, phenomenon until a region is reached in the neighborhood between a 2 and 3% sulfur content, when the surface of the product is no longer sticky. At the same time the product becomes tougher and does not rupture readily on stretching. At this stage the product is said to be completely vulcanized. If heated too long, it becomes comparatively brittle and it is then said to be overvulcanized. When the various vulcanizates, mentioned above, are subjected to peptization with benzene, it is found that the low sulfur vulcanizates can be peptized completely and, as the sulfur content increases, it gradually becomes more difficult for the benzene to peptize the product completely. A stage is reached finally when some of the product can be peptized while the rest remains behind in the form of a swollen mass resembling solidified gelatin. And thus, as the sulfur percentage of the vulcanizate increases, less of the product is peptized by the benzene, until a stage is reached at which practically no peptization takes place. The benzene simply swells the rubber product Stevens[20] has shown that even with vulcanized products containing as high as 8.64% combined sulfur it was possible to peptize only about 13% of the product with benzene. It therefore follows naturally that complete insolubility in benzene must take place at a coefficient of vulcanization much higher than that just mentioned.

No matter what the method used in vulcanizing the product, there has always taken place a very strong union between all the rubber and some of the vulcanizing agent. All efforts to disrupt this union have resulted in complete annihilation of the rubber molecule. If a soft rubber vulcanizate be prepared, it is possible to add a halogen until the difference between its stoichiometric composition and that of the upper limit hard rubber compound $(C_5H_8S)_n$ is satisfied. This would tend to indicate that the combined sulfur in the soft rubber product is held in chemical union.

Whenever rubber is rolled on the mill, it becomes softer and more plastic. It is also peptized more rapidly by the ordinary solvents. After being milled the rubber is said to have become "depolymerized." Sulfur is known to be fairly soluble in rubber at vulcanization temperatures, and as vulcanization proceeds the sulfur becomes more soluble.

In studying the subject of vulcanization one should bear in mind improvements in the physical properties of a vulcanizate due to the presence of various fillers. Clays and various forms of carbon black are commonly used in the rubber industry. It has been observed that the particle size and the method used in preparation of the filler have an important bearing on the final physical properties of the vulcanizate. The method used in preparation of fillers has undoubtedly an important effect on their surface characteristics. Carbon blacks are used in tread stocks and are known to improve the strength and the abrasive qualities of the vulcanizate. This is probably due to the peculiar properties of surface adsorption common to various forms of carbon black. In this connection it might be mentioned that the use of accelerators improves the physical properties of the vulcanizate. This effect has not been ascribed to surface phenomena, but to the fact that less heat is used in vulcanization when accelerators are present. Heat has a degenerating effect on a vulcanized product and naturally the less heat used in the process the more improved are the physical properties of the product.

In addition to the above facts, one must remember that it is possible, with the presence of powerful accelerators, to effect vulcanization even with coefficients of vulcanization less than 0.5% sulfur.

A knowledge of the ultimate structure of the rubber latex particle ought to be

[20] *J. Soc. Chem. Ind.*, **38**, 195T (1919).

of some help in studying the subject of vulcanization. The latest work of Hauser[21] has shown that the latex globule consists of an outer skin, a solid phase, evidently a high polymer of isoprene, and an inner liquid phase, evidently a lower polymer of the same hydrocarbon. Outside of the polymerized hydrocarbon skin is a layer of protein which plays the leading role in the coagulation process. It is interesting to note that X-ray researches on rubber have always indicated the presence of an amorphous phase. When the rubber is stretched, the presence of crystalline phase is also indicated. The presence of this phase is said to be due to the highly polymerized outer layer of the latex globule.

Although the formulation of the adsorption theory caused a great deal of activity in rubber research, nevertheless, the problem of vulcanization was not attacked in a comprehensive manner. Investigators have studied the various facts upon which both the adsorption theory and Weber's theory are based, but no attempt has so far been made by any single individual to study the vulcanization problem from every conceivable viewpoint. A person who has investigated a problem from all angles is always in position to have a better perspective view of the situation than one who has limited himself to a single phase of the question. His position enables him to weigh his evidence properly so that his final judgment becomes quite more reliable. Even Wolfgang Ostwald was forced to make some blunders in formulating his adsorption theory since he had done very little work on vulcanization and naturally was in no position to be able to weigh his evidence properly. The work undertaken in this investigation has been done with the idea of testing thoroughly every theoretical possibility that might be used in formulating a satisfactory vulcanization hypothesis.

Let us now consider all the theoretical assumptions that might be associated with a proper explanation of the vulcanization process. In the first place, we might think of the sulfur-rubber combination as simply a case of solid solution. If such be the case, it should be possible to extract some of the combined sulfur by treating the vulcanizate with an excess of raw rubber in a suitable solvent. We might also consider the process as simply adsorption or a combination of adsorption and a chemical compound. Either possibility could be verified by the same set of experiments. In either case, heterogeneity should become apparent whenever the soft rubber vulcanizate is subjected to fractional peptization in benzene. The first fractions to be peptized should show a low content of sulfur, while those following should naturally show a higher sulfur content. The reverse process of synthesizing a vulcanized product from raw rubber and a sample containing a high coefficient of vulcanization should likewise naturally follow. It is also possible to assume that the nature of the rubber is changed during the process of vulcanization and that the sulfur-rubber combination is simply a side issue. In that case, it should be possible to induce the change of vulcanization without any apparent participation on the part of the vulcanizing agent. So far, this has never been realized. Furthermore, it should be possible to reverse the change by obtaining raw rubber from vulcanized rubber; but this, likewise, has never been effected. As far as experimental evidence is concerned, we might just as well rule this possibility out. We might also look upon the rubber molecule as an unusually large one and capable of forming a series of compounds with sulfur. Let us assume the molecule of rubber to be $(C_{10}H_{16})_n$, in which n happens to be very large. This is capable of combining with a small percentage of sulfur to form the compound $(C_{10}H_{16})_nS_2$. Further increase of the percentage of sulfur will produce the combination of $(C_{10}H_{16})_n(S_2)_2$, and thus progressively down the line until the maximum amount of sulfur is taken up with the production of the com-

[21] *Ind. Eng. Chem.*, **18**, 1146 (1926).

pound $(C_{10}H_{16})_n(S_2)_n$. If we should take n large enough the difference in properties of the various compounds would be so small as to preclude any possibility of separation. Thus there would be no abrupt changes in the physical properties of the products and all changes in properties would take place practically continuously. The above assumptions would be very difficult to check experimentally; but if, by chance, compounds happened to be formed at half per cent intervals, or greater, it might be possible to notice some flat portions in the curve by studying the equilibrium relations between rubber and sulfur dissolved in some solvent in which the rubber is not appreciably peptized. We are now ready to proceed to the body of the investigation in which the above theoretical possibilities have been submitted to experimental verification.

Experimental Data

The various experiments performed during this investigation will not be discussed in chronological order, but will be grouped together under the respective theories which they are designed to verify. Before describing the test for solid solutions, it would be well to detail the analytical procedure in the determination of sulfur in samples of vulcanized rubber. The author has used this method extensively for the determination of combined sulfur and has found it to be quite reliable.

A 0.5 gram sample of extraction residue is placed in a 300 cc. sulfur flask and 15 cc. of saturated solution of arsenic acid is added. The saturated solution of arsenic acid is made by adding arsenic pentoxide to boiling water until the boiling point of the solution is 140° C. After the arsenic acid addition, 13 cc. of fuming nitric acid, which has been standing over an excess of bromine, is added to the sample. The mixture is covered with a watch-glass and boiled on a hot plate until the sample is completely oxidized so that a clear solution is obtained, and, if necessary, more acid is added. The watch-glass is then removed, the contents evaporated to a sirup, and some crystals of potassium chlorate are added to expel the oxides of nitrogen. The evaporation is continued almost to dryness, cooled, and the residue is then taken up with 50 cc. of hydrochloric acid (1:10). The flask is warmed until solution becomes complete, filtered, diluted to about 250 cc., and precipitated with barium chloride. The barium sulfate is filtered, ignited and weighed in the usual manner. Blank runs should always be made on new lots of arsenic acid.

Test for Solid Solution

If the sulfur-rubber combination existed in the form of a firm solid solution, it should be possible to extract some of the sulfur by treating the vulcanizate with solvents in which the sulfur would be readily soluble.

Accordingly 3 grams of the extracted hard rubber, prepared as described in the next section, were added to 50 cc. of aniline which contained 6 grams of raw rubber. Whenever the word "extracted" is used, it is understood to imply extraction with acetone. Aniline was chosen for the solvent because sulfur is very soluble in hot aniline and the latter is quite effective in peptizing raw rubber. The raw rubber was added to make the extraction more effective. It was thought that the raw rubber would combine with the sulfur extracted by the aniline, thus renewing the solvent action of the latter. The entire mixture was kept in a pressure bottle for fifty hours at a temperature of 190° C. The hard rubber had been previously extracted thoroughly with acetone so that no free sulfur was present. The hot solution was then filtered several times and the filtrate evaporated to dryness. The sulfur content of the evaporated residue was then determined.

Although the total amount of hard rubber present contained 0.6 gram of sulfur nevertheless there was only 0.04 gram sulfur left in the filtrate residue. The presence of the 0.04 gram sulfur was undoubtedly due to the passage of some of the hard rubber particles through the filter paper. It is known that hot aniline is capable of peptizing hard rubber shavings to a certain extent.

Under the conditions of the experiment, sulfur is known to be very soluble in aniline, and since none of it had passed into the aniline-raw rubber mixture, it stands to reason that the sulfur in the hard rubber is held in a union that is firmer than one would expect from a solid solution. Hence this experiment proves the assumption of a solid solution as a theory of vulcanization to be untenable.

Tests for Adsorption and Chemical Compound Adsorption Complexes

Mixtures without Accelerators.—As mentioned in the introduction, the same type of experiments could be used to verify either of the above assumptions. Let us assume that a chemical compound is formed which corresponds to the product obtained as the upper limit compound in hard rubber, *viz.*, $C_{10}H_{16}S_2$. The compound thus formed is either adsorbed by the rest of the raw rubber, or the latter is adsorbed by the compound, thus forming an adsorption complex that gives to the rubber product the property known as vulcanization. It can be seen from this hypothesis that it should be possible, starting with a mixture of 15 per cent hard rubber and 85 per cent raw rubber, and subjecting the same to a process that would encourage adsorption, to realize finally a vulcanized product.

Accordingly 70 parts of pale crepe rubber were mixed with 30 parts of sulfur on a hand roller mill that had been designed for the purpose of rolling sheet metal. Although this was far from being an ideal method for preparing rubber batches, yet it served its purpose admirably. The mixture was then cured in a steel mould for 12 hours at 145° C. The hard rubber, thus prepared, was broken up into fine shavings by means of an emery wheel and then thoroughly extracted for one week with acetone in a Soxhlet apparatus. A mixture of 15 parts of the hard rubber raspings and 85 parts of raw rubber was made on the roller mill, and though it was kept in a steel mould for 21 hours at 150° C., it showed none of the physical properties of a vulcanized product. In fact, it was possible to separate the hard rubber from the raw rubber by peptization in benzene.

It was thought advisable to repeat the experiment using a solvent that can peptize both raw and hard rubber. Xylene was tried first, but it was impossible to peptize the hard rubber. Cresol was then tested and found to be successful.

One and one-half grams of hard rubber were peptized in 125 cc. of cresol by means of vigorous stirring and heating for 4 hours at the temperature of boiling cresol (about 194° C.). Eight and a half grams of raw pale crepe were peptized in 75 cc. of cresol by stirring and heating at 150° C. for 3 hours. While the latter was still hot, it was poured into the peptized hard rubber solution and the mixed sol was stirred continuously and heated at 160–170° C. for 36 hours in an effort to cause vulcanization. The solvent was then distilled off at reduced pressure, most of it going off at a temperature of 95° C. (pressure of 15 mm. of mercury). The last traces of the solvent were difficult to eliminate, so that it was necessary to keep the oil bath at a temperature of 184–210° C. for about 12 hours. On opening the apparatus, the bottom of the flask contained a hard, black, vitreous mass that looked like bakelite. The total weight of the product exceeded the entire amount of the mixture that had originally been placed in the flask. Since a small stream of air had been bubbled through the flask during the distillation in order to prevent bumping, it is conceivable that oxidation might have taken place with the resulting formation of the resin. Accordingly, the experiment

was repeated without allowing any air to bubble through the flask, but even then the same type of resin was obtained at the end of the experiment. Obviously the resin formation cannot be ascribed to oxidation by the air.

It was thought that the resin formation might possibly be due to the condensation of the rubber hydrocarbon with the cresol. Therefore the experiment was repeated with just raw rubber and cresol. The result obtained was different from that observed in the initial experiment. It proved to be a viscous semi-solid. The fact that the product was different showed that something had not been considered. When cresol is heated with sulfur or sulfides it is capable of forming a dye. Hence it was immediately assumed that the formation of the resin depended on the presence of sulfur.

It was known from previous experiments that pure pale crepe and cresol did not produce a resin after the evaporation of the solvent. Likewise a mixture of hard rubber, raw rubber and cresol, after subsequent evaporation, did not produce a resin. Since sulfur was known to combine with cresol, it was thought that this combination plus raw rubber was responsible for the resin formation. Therefore, it ought to be possible to produce the resin by making a mixture of raw rubber, sulfur and cresol, followed by distillation of the solvent. The product obtained in this manner was an amber-colored resin, similar to the one obtained in the previous experiment. Hence it was thought that the presence of sulfur was the cause of the resin. Accordingly, it was decided to extract all the hard rubber thoroughly. Hard rubber raspings were heated under reduced pressure so that the free sulfur was condensed on cool parts of the flask. This was continued for 36 hours, followed by extraction in a Soxhlet with carbon disulfide for 100 hours. Thereupon it was followed by acetone extraction for 48 hours.

The thoroughly extracted hard rubber was now used in a 15–85 hard rubber, raw rubber mixture that was peptized in cresol. The procedure was the same as in the former experiments; likewise the result was the same. A similar experiment was performed, using a thoroughly extracted sample of soft rubber instead of the hard. The soft rubber had been made from a 7 per cent sulfur-rubber mixture. Here, likewise, the same type of resin was obtained. Naturally, it was concluded that the resin formation was due, perhaps, to the reaction between the rubber sulfide compound and the cresol or to the reaction between the cresol and free sulfur formed by the possible decomposition of the vulcanized rubber. The next experiment was therefore performed to see whether hard rubber decomposes at 190° C., forming free sulfur.

A sample of hard rubber was extracted with acetone for one week and then analyzed for its sulfur content. The sample was then heated to 190° C. for one week in a flask at the reduced pressure. This flask contained a condenser that would collect any free sulfur formed. After this prolonged heating, the sample was again extracted with acetone for one week and analyzed for its sulfur content. No change in the amount of combined sulfur was noticeable. Evidently no decomposition took place when the hard rubber was heated.

It was thought desirable to see what would happen when just sulfur and cresol were heated together, with subsequent evaporation of the solvent. The final product was a resin similar to those obtained in all the previous cases. The distillate had a strong-mercaptan odour. The resin was essentially a mixture of sulfur and tar together with a small amount of organic thiocompounds that would have been converted into a brown sulfur dye had the mixture been subjected to much more prolonged heating. When treated with acetone, the sulfur dissolved and a soft, viscous, semi-solid was left which was similar to the residue remaining when cresol alone was distilled. Thus the resin obtained in all the previous experiments was

simply a mixture of tar due to the cresol and whatever else happened to be in the solution. Since the resin was not a homogeneous product, probably no vulcanization had taken place and resort was made to other solvents in an effort to find one in which the residue could be more easily identified. Attempts were made to precipitate the rubber in cresol by adding other solvents, but these were rather unsuccessful. Alcohol, acetone, benzene, chloroform, acetic acid, methylalcohol, carbon tetrachloride, toluene and tetrachlorethane were tried, but none of them proved to be effective. Later in this investigation some experiments were performed in which it was possible to precipitate most of the rubber by the use of absolute alcohol and potassium hydroxide.

Cresol having proved troublesome, other solvents were tried, and it was found that hot aniline could peptize hard rubber shavings. The sol obtained in this case is not as finely divided as the one obtained with raw rubber in benzene, but, nevertheless, it was a colloidal suspension. A sol of hard rubber in aniline was treated with one of raw rubber with the ratio of 15 parts of hard rubber to 85 parts of raw rubber. The mixture was stirred vigorously for 20 hours at 180° C. and subsequently distilled at reduced pressure. The dark, gummy product did not appear to be vulcanized. When peptized with benzene the hard rubber settled out, showing that no vulcanization had taken place. Another experiment was tried in which a 15–85 mixture of hard and raw rubber was heated under pressure for 4 hours until the temperature was raised as high as 245° C. This is about 60 degrees above the boiling point of aniline. On examining the contents of the tube, the particles of hard rubber were found to be dispersed in the raw rubber gel. The aniline was evaporated off. The residue did not appear to be vulcanized and the raw rubber was separated by means of peptization in benzene. The above experiments seem to indicate that one cannot obtain a vulcanized product from mixtures of hard and raw rubber subjected to the treatment outlined above.

In this connection it might be appropriate to mention a very interesting series of experiments performed by Weber[22] in 1894. This investigator performed experiments similar to those outlined above with the exception that, instead of hard rubber, he used the end product obtained when raw rubber is treated with an excess of sulfur chloride.

Weber dissolved five grams of Para rubber in 1000 cc. of benzene. To this he added 5 grams of sulfur chloride . In consequence of the great dilution, the reaction proceeded slowly, but after 3 hours standing all the sulfur chloride had disappeared. The solution was left standing overnight and on the following morning 400 cc. of it, representing two grams of raw rubber used, were treated with absolute alcohol and the polyprene sulfochloride that separated out was purified and analyzed. It contained 23.78% sulfur, so that there was no doubt but that the rubber was converted into the sulfochloride, $C_{10}H_{16}S_2Cl_2$, even in such a dilute solution.

To the remaining 600 cc. of the above solution, 22.5 grams of pure rubber in 200 cc. of benzene were now added, and the mixture strongly agitated. The gelatinous character of the mixture rapidly changed into that of an ordinary rubber solution. On pouring this solution into absolute alcohol, a voluminous precipitate very much like polyprene sulfochloride was obtained. This precipitate was separated from the supernatant liquid by filtration, the filtered residue repeatedly washed with warm alcohol, and then dried *in vacuo*. In this manner a rather elastic substance was obtained, which on analysis was found to contain 4.96% sulfur.

The question now arises whether this product really possesses the properties of vulcanized rubber. To determine this point the substance was placed in benzene. After 18 hours, complete solution has taken place, the solution appearing somewhat

[22] *J. Soc. Chem. Ind.*, **13**, 14 (1894).

turbid. It was strongly diluted and filtered through a hot water funnel. The filtrate appeared to be clean. On the filter remained a residue that was repeatedly washed with warm benzene and then dried. It formed a whitish, easily friable mass that contained 23.44% sulfur on analysis. There is no doubt that this substance represents the total quantity of polyprene sulfochloride that was mixed with the rubber, and this is further confirmed by the fact that the above mentioned filtrate contains not the slightest trace of chlorine or sulfur. "This result," as Weber stated, "is conclusive proof that a mixture of polyprene sulfochloride and rubber possesses the properties to be anticipated for such a mixture, but *not* those of vulcanized rubber." He went ahead further and proved that a rubber product vulcanized with sulfur chloride so that the combined sulfur amounted to only 5 per cent, was a homogeneous compound and behaved differently from the mixture that he obtained above.

For this purpose, 25.5 grams of pure Para rubber were dissolved in 100 cc. of pure benzene. Three grams of sulfur chloride were added to this solution, mixed vigorously, and then left to stand. Very soon the mass began to thicken, the reaction reaching its maximum after 15 minutes. After several hours' standing, the jelly was thoroughly broken up by stirring, and the resulting pulp poured into absolute alcohol. The precipitate was filtered, the occluded benzene driven off, and the substance finally dried *in vacuo*. The dry product contained 5.11% sulfur, and in this respect is therefore identical with the mixture of polyprene sulfochloride and rubber. The elasticity of the new substance is far superior to that of the mixture, from which it further differs by its absolute insolubility in all solvents. Even an immersion of weeks at a time fails to soften it although considerable swelling takes place. This, however, is also the case with the sulfochloride $C_{10}H_{16}S_2Cl_2$. "It is evident," said Weber, "that this substance containing only 5 per cent sulfur has no unaltered rubber and must be considered as a sulfochloride distinctly different from $C_{10}H_{16}S_2Cl_2$."

Mixtures Containing Accelerators.—Thus far all the experiments have been performed without the use of any accelerators. Since accelerators are quite effective in facilitating vulcanization, it stands to reason that it would be a good idea to add them to mixtures of the type that we have been studying in an effort to see whether any desirable effect might be induced. Most accelerators act more effectively in conjunction with zinc oxide, hence the latter was added to some of the mixtures.

About 12.75 grams of pale crepe were mixed with 2.25 grams of extracted hard rubber raspings on the roller mill, and the resulting product divided into six portions. To each 2.5 gram sample of the hard raw rubber mixture were added zinc oxide and the various accelerators as shown in Table I.

"Grasselerator 808" is an accelerator containing no sulfur; it is butylideneaniline.

D.O.T.G. is di-ortho-tolyl-guanidine.

"Monex" is an ultra-accelerator: tetramethylthiourammonosulfide.

TABLE I

Sample No. 1.....	6% Grasselerator 808 (0.15 g.) and 6% zinc oxide
Sample No. 2.....	6% Grasselerator 808 and no zinc oxide
Sample No. 3.....	6% di-*o*-tolylguanidine and 6% zinc oxide
Sample No. 4.....	6% di-*o*-tolylguanidine and no zinc oxide
Sample No. 5.....	6% Monex and 6% zinc oxide
Sample No. 6.....	6% Monex and no zinc oxide

All the ingredients outlined above were mixed in separate batches on the roller mill. These were placed in a steel mould and heated at 140° C. for 3 hours to

see whether any vulcanization would take place. All the samples failed to exhibit the physical properties of a vulcanized sample. When peptized in benzene, the zinc oxide and the hard rubber settled to the bottom of the flask.

The next step was to see whether the same samples could be vulcanized in solution. Two gram portions of each of the six samples were respectively peptized in 20 cc. of cresol. They were heated for 24 hours at a temperature of 150–170°. Seventy-five cc. of absolute alcohol were added to each of the samples in an effort to precipitate the peptized rubber. It was found that the hard rubber and zinc oxide were thrown out of suspension, but that the raw rubber remained in colloidal solution. The hard rubber and zinc oxide were filtered off and 20 cc. of a concentrated solution of potassium hydroxide were added to each of the filtrates in an effort to coagulate the raw rubber. It was possible in this way to precipitate some of the raw rubber, but not all of it.

Since all the ingredients in the above mixtures could be separated, undoubtedly no vulcanization had taken place.

The above series of experiments were repeated, using a soft vulcanized rubber instead of hard rubber. Two parts of raw rubber were mixed with 1 part of soft rubber containing 2.8% sulfur (combined). Accelerator and zinc oxide were added in the same proportions as in the previous set of experiments. The results obtained were likewise similar to those obtained with the hard rubber mixtures.

Fractional Peptization Tests

If, during the process of vulcanization, compounds are formed between sulfur and rubber, it should be possible to test the homogeneity of the product by fractional peptization. The first fractions should have percentages of sulfur that differ from those which follow. Hence it ought to be possible to separate a vulcanized product into the supposedly unattacked raw rubber and the product resulting from the chemical union between the sulfur and the hydrocarbon. Some work along this line has been done by Stevens,[23] but he did not go far enough. The lowest combined sulfur content in his vulcanizate was 3.8 per cent. He extracted his vulcanizate sample exhaustively with benzene for one week and determined the proportion of the sample dissolved by the benzene. The sulfur present in the sample before extraction and that left after extraction was determined. The following result was obtained:—

Proportion dissolved by benzine	Before extraction	Sulfur content after extraction
30.8%	3.80%	3.85%

These results show that the vulcanized product is homogeneous as far as the sulfur content is concerned; the peptized portion containing the same amount of sulfur as that which was left after extraction. The question now arises whether this homogeneity will persist with vulcanized products containing much less combined sulfur than the sample studied by Stevens. With this in view, the following rubber mixtures were prepared:—

Thirty grams of pale crepe were mixed on the roller mill with 0.6 gram of accelerator (about 2% of Grasselerator 808). The resulting mixture was divided into 4 portions. To the first 5 gram portion was added 0.075 gram of sulfur, the resulting mixture being worked on the roller mill. This corresponds to an approximate sulfur content of 1.5 per cent.

The second 5 gram portion was treated in a like manner with 0.05 gram of sulfur (about 1 per cent).

[23] *J. Soc. Chem. Ind.*, **38**, 195T (1919).

The third 5 gram portion was mixed with 0.025 gram of sulfur (about 0.5 per cent).

The last portion, amounting to 15 grams, was treated with 0.015 gram of sulfur (about 0.1 per cent).

All of the above portions were vulcanized in a steel mould for 5 hours at a temperature of 140–150° C. The samples were then extracted for 2 days with acetone to remove all the free sulfur.

A day after the extraction the batches were heated in the oven at 100° C. to make certain that all the acetone had been driven off. The samples were then analyzed for their respective combined sulfur values. Each of the above batches was then placed in a Soxhlet apparatus and subjected to peptization by hot benzene. Various fractions were thus obtained and each of these was dried free of solvent and the sulfur content determined. The results obtained are given in Table II.

TABLE II

	Original sample	First fraction	Second fraction	Third fraction
Weight of sample analyzed	0.5000 g.	0.5488 g.	0.3235 g.	0.2283 g.
% Sulfur	1.42	1.37	1.30	1.39
	Second Sample			
Weight of sample analyzed	0.5405 g.	0.4980 g.	0.3524 g.	0.4100 g.
% Sulfur	0.75	0.72	0.80	0.77
	Third Sample			
Weight of sample analyzed	1.0139	0.7192		0.8024
% Sulfur	0.43	0.42		0.39
	Fourth Sample			
Weight of sample analyzed	3.9250	3.6072	3.7638	4.4677
% Sulfur	0.091	0.09	0.08	0.085

The above results show that homogeneity as far as sulfur content is concerned persists even with samples containing less than 0.1% of combined sulfur. To be sure, all of the "vulcanized" products shown in the previous tables did not exhibit the physical properties common to a completely cured product. All the samples were heated for 5 hours at a temperature between 140 and 150° C. This is more than sufficient to vulcanize any product, but since they did not contain sufficient sulfur, they appeared to be undercured, even though the sulfur which they did contain was in complete union with the rubber. Such being the case, it was thought advisable to verify Weber's contention that the properties of vulcanization first become apparent at a vulcanization coefficient of from 2 to 2.5 per cent.

Accordingly, three samples were prepared, each of which contained about 2% accelerator (Grasselerator 808). About 2 % sulfur was added to the first sample, 2.5% to the second, and about 3% to the third. All were heated in a steel mould at a temperature of 140–150° C. for 5 hours. The samples were taken out for examination, and it was noticed that the one containing about 3% sulfur was definitely overcured. The other two cases were doubtful. It was known definitely that a sample containing 1.5% sulfur appeared undercured under similar circumstances, and since the 3% sample was overcured, Weber was right in his contention that signs of vulcanization are first noticeable with samples when they contain from 2 to 2.5% sulfur. Although Weber is probably correct when the samples which are free from any powerful accelerators are considered, nevertheless it has been possible in this laboratory to produce with the aid of zinc oxide and ultra-accelerators vulcanized samples of rubber that were cured at boiling water temperature and contained a sulfur content slightly less than 0.5 per cent.

Experiments with Protein-Free Rubber

Since each globule in a piece of rubber is surrounded by a film of protein, it was thought that adsorption might take place much more readily if no protein were present. Therefore steps were taken to prepare some protein-free rubber. The rubber was first extracted thoroughly in acetone for one week. Then it was placed in petroleum ether and allowed to stand quietly so that the hydrocarbon was slowly peptized. From time to time the supernatant liquid was siphoned off carefully and evaporated to dryness. The rubber prepared was free from protein, but the process used was a very tedious one. It is much easier to dissolve the rubber in chloroform and to precipitate the hydrocarbon with alcohol. A sample of this protein-free rubber was mixed with sulfur and vulcanized so that the coefficient of vulcanization was about 2.8 per cent. A gram of this vulcanizate was peptized in hot aniline and then a gram of raw rubber was added to the solvent and thoroughly mixed. The mixed sol was heated at the boiling temperature of aniline for 24 hours, after which the solvent was evaporated off at reduced pressure. The residue was then subjected to fractional peptization in benzene. The following results were obtained:

	Weight of sample (Grams)	% Sulfur
First fraction	0.4188	1.1
Second fraction	0.311	1.4
Third fraction	0.4945	1.8
Fourth fraction	0.241	2.0

The results of the above experiments show that the residue was not homogeneous and that the protein extraction was of no avail for inducing vulcanization between mixtures of raw and cured rubber.

Rubber Mixtures with Closely Related Coefficients of Vulcanization

Heretofore, the components of the rubber mixtures used consisted of widely divergent coefficients of vulcanization. Raw rubber having a zero coefficient was mixed with hard rubber having a coefficient somewhere above 20 per cent. Of course, when soft rubber mixtures were treated, the coefficients were much more closely related, but still there was quite a difference. Hence, it was thought desirable to test some mixtures in which the coefficients did not differ by more than 0.5 per cent. Accordingly, two rubber batches were prepared which showed after vulcanization the following percentages of combined sulfur:

No. 1	0.37% sulfur
No. 2	0.57% sulfur

Five grams of the first sample were peptized together with an equal amount of raw rubber in boiling xylene and refluxed for 3 days. The solvent was then distilled off and the residue subjected to fractional peptization with benzene. Likewise, 5 grams of the first batch were similarly treated with 5 grams of the second vulcanizate and the peptized mixture refluxed for 3 days in xylene. Here, likewise, the solvent was distilled off and the residue subjected to the same treatment as in the previous case. The following results were obtained:

	Mixture of raw rubber and 0.37% vulcanizate	Mixture of 0.37% and 0.57% vulcanizates
First fraction	0.13% sulfur	0.38% sulfur
Second fraction	0.17% sulfur	0.39% sulfur
Third fraction	0.34% sulfur	0.47% sulfur
Fourth fraction	0.35% sulfur	0.54% sulfur

The above results clearly show that even in cases such as listed above in which the coefficients of vulcanization are very closely related, it is impossible to produce a homogeneous product from mixtures. Even in the last mixture in which the coefficients differed by only 0.2 per cent, it was quite obvious that the product lacked homogeneity and that separation had occurred.

Fractional Peptization with Low Temperature Vulcanizates

Since the average vulcanization temperature is far above the melting point of sulfur, the latter is in a liquid state previous to its reaction with the rubber. The fact that it is in a liquid state helps it to diffuse through the rubber more readily and thus distribute itself uniformly throughout the rubber before actual vulcanization sets in. It was thought that if vulcanization could be induced at a temperature below the melting point of sulfur, it might be possible to produce a heterogeneous product in which parts of the rubber in close proximity to particles of solid sulfur would be more vulcanized than other regions. In order to produce vulcanization at a temperature of boiling water, it was found necessary to mix the rubber with about 3% zinc oxide and 0.25% of an ultra-accelerator such as tetramethylthiourammonosulfide. About 0.5% of sulfur was used in the above mixture. Part of the above batch was cured for 30 minutes in boiling water, and the other part was cured at the same temperature for 1.75 hours. If the time of vulcanization was continued for 2.5 hours, the sample became fully cured. That is, the physical properties of a completely vulcanized sample became apparent. After vulcanization the samples were extracted with acetone for 2 days and then subjected to fractional peptization in benzene. The results were as follows:

	30 min. cure	105 min. cure
First fraction	0.21% sulfur	0.51% sulfur
Second fraction	0.19% sulfur	0.51% sulfur

These data show that in both cases the products are homogeneous and that the sulfur is quite soluble in the rubber even at temperatures below its melting point. The natural corollary of this experiment is that sulfur in the solid state does not react with rubber. It reacts with the rubber when it is either in solution or in the vapor phase.

Test for Giant Molecule

It is theoretically possible to consider an entire piece of rubber as one huge molecule. If such be the case, it should be possible, when a piece of new rubber is covered with sulfur and vulcanized, to establish heterogeneity in the product by cutting it into various sections, as one would do with a knife. Some of the sections, thus separated, should show very high percentages of combined sulfur, while other parts should be practically free of any sulfur. On the other hand, if such a product were to be tested by means of fractional peptization in solvents, it would be impossible to peptize part of the giant molecule-sulfur compound without peptizing it all. In other words, all the various fractions of peptization must show the same sulfur content.

In order to verify the above assumption, 15 grams of rubber were rolled into a sheet of about $^3/_{16}$ inch thickness. The upper surface of this sheet was covered with 4 grams of sulfur which was equivalent to 30% of the weight of th rubber used. The sheet was then placed in a steel mould and vulcanized at 150° C. for 3 hours. After vulcanization, samples for analysis were taken from the upper and lower surfaces of the vulcanizate. They were first extracted with acetone and then analyzed for combined sulfur. The sample from the upper surface showed a vulcaniza-

tion coefficient of 9.5, while that of the lower surface could only boast a mere 3.2. When submitted to fractional peptization, this product could be separated into fractions, containing radically varying amounts of combined sulfur. The fact that heterogeneity was apparent when the product was submitted to fractional peptization is proof that the assumption of considering a piece of rubber as a giant molecule is untenable.

Tests for Chemical Compounds

Thus far, we have studied the problem of vulcanization from every conceivable angle, but have not as yet attacked the problem of the equilibrium relations existing between raw rubber and sulfur dissolved in a suitable solvent. In fact the only experiments that have been performed along this line were confined to a study of the amount of sulfur taken up by raw rubber from a bath of molten sulfur. In this case, equilibrium resulted with the formation of the hard rubber compound, $C_{10}H_{16}S_2$, containing 32% sulfur. For the success of this experiment, it was essential to find a solvent capable of dissolving sulfur but at the same time being void of any peptizing effect on raw rubber. Normal butyl alcohol, although not ideal, proved to be the best available solvent for this purpose. At the boiling point of butyl alcohol, the rubber softens and is very slightly peptized, nevertheless it served the purpose.

About 20 grams of raw rubber were extracted exhaustively with acetone. It was thought best to free the rubber from all resins so that a study could be made of the equilibrium relations between the sulfur and the rubber without the presence of the disturbing influence of the resins. Realizing that it would take very long for equilibrium to be reached at the temperature used in the experiment, 0.4 gram of accelerator (Grasselerator 808) was used. This was mixed with the 20 grams of extracted rubber on a roller mill, and drawn out into thin sheets of about 2 mm. thickness. These sheets were cut into strips of about 3 to 4 mm. in width. Half-gram samples of these strips were weighed carefully, and wrapped around glass drums. While wrapping, the strips were stretched to provide more surface, with the net result that their final thickness amounted to about 1 mm. Each of the glass drums containing half gram samples of rubber was placed in a long tube (200 by 20 mm.), each of which contained 30 cc. of *n*-butyl alcohol. After the necessary amount of sulfur had been added to each test tube, they were sealed off and placed in a *n*-butyl alcohol bath that was continuously refluxing so that a constant temperature of 117° C. was maintained. Table III shows the concentration of ingredients used in the various test tubes:

TABLE III

Each of the test tubes contained 30 cc. of *n*-butyl alcohol and 0.5 gram of rubber

5 tubes contained	0.01 gram of sulfur each
4 tubes contained	0.025 gram of sulfur each
4 tubes contained	0.06 gram of sulfur each
4 tubes contained	0.12 gram of sulfur each
4 tubes contained	0.2 gram of sulfur each
5 tubes contained	0.5 gram of sulfur each

After the first week's refluxing in the *n*-butyl alcohol bath, some of the samples were analyzed to see how much sulfur had been taken up from the solution by the rubber. These test tubes were to be taken out from time to time and analyzed to see whether or not equilibrium had been attained. The samples taken out for analysis were treated as follows:

On cooling, the test tubes were opened, the solvent distilled off at reduced pres-

sure, so that the temperatures of distillation were less than that of the boiling butyl alcohol (117° C.). Otherwise, the equilibrium might be disturbed if too high a temperature of distillation were used. The sample was then extracted with acetone for 2 days to remove all the free sulfur. The rubber was then analyzed for the combined sulfur content.

After the first week's refluxing, a sample of the tubes containing the largest amount of sulfur showed on analysis that enough sulfur had been taken up to form a vulcanizate with a combined sulfur content of 29%. After three weeks' refluxing, another sample of the same type showed 32.4% sulfur. In other words, the sample had already reached the upper limit of chemical combination.

In a like manner, after the first week, a sample of the tubes containing the smallest amount of sulfur showed that the rubber had taken up 0.0048 gram of sulfur. This is slightly less than 0.5 the available sulfur present (0.01 gram). After 3 weeks it showed 0.0081 gram of sulfur in combination. A month later another sample of the same tubes was analyzed and showed a value which was just slightly less than the previous value reported. Obviously, equilibrium had already been attained. It took a longer time for the other concentrations to reach equilibrium, but all of them reached this point finally within the time used for refluxing the samples. Some of the samples were refluxing for about two and one-half months. As they became more highly vulcanized, the rate of diffusion of the sulfur was correspondingly decreased, so that it may finally have become slow enough not to be noticeable, although true equilibrium had not been attained. Thus no one could say with certainty whether or not true equilibrium had been reached. Venable and Green have reported that, in their determinations of solubilities of sulfur in rubber by diffusion of pure sulfur, it was impossible to obtain any solubility values with coefficients of vulcanization beyond 7 per cent, since the rate of diffusion of sulfur became practically zero.

The rubber samples were wrapped around the glass drums to provide greater surface area, but this was entirely nullified during the long process of hearing, since all the rubber gradually sagged to the bottom of the test tube. Probably some of it had been peptized. This likewise slowed up the process of sulfur diffusion. The test tubes with the largest concentration of sulfur had more of it than necessary to saturate the 30 cc. of *n*-butyl alcohol, whereas the others were able to dissolve their quota of sulfur without leaving any excess at the bottom. The following are the equilibrium values obtained with the various concentrations used in the experiments:

TABLE IV

Initial amount of sulfur in tube	Conc. per cc. of alcohol	Amount of sulfur combined	Contained S per gram of rubber
0.01 gram	0.00033	0.008	0.016
0.25	0.00083	0.020	0.040
0.06	0.002	0.045	0.090
0.12	0.004	0.080	0.160
0.2	0.0067	0.127	0.254
0.5	0.0167	0.242	0.484

Each sample contained 0.5 gram rubber and 30 cc. of *n*-butyl alcohol besides the various amounts of sulfur as indicated in Table IV.

In Fig. 1 the amounts of combined sulfur per gram of rubber are plotted against the initial concentration of the sulfur in the alcoholic solution. The curve obtained starts out as a perfectly straight line and then bends very slightly away from the vertical axis. It continues, undoubtedly, until it strikes the horizontal line indicat-

ing the upper limit hard rubber compound containing 32% sulfur. It is regrettable that so few high concentrations had been selected in planning the experiment. Otherwise the curve would have appeared much more complete in that region.

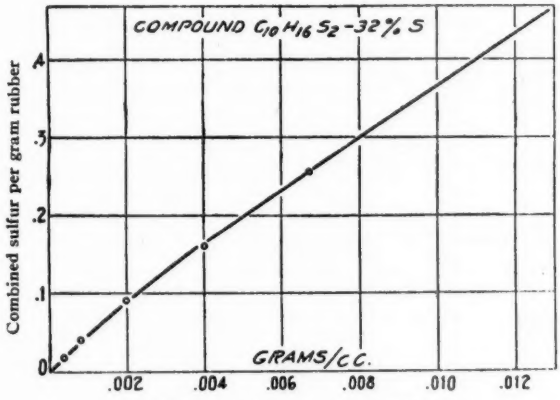


Figure 1

There is only one point to indicate the formation of the upper limit compound $C_{10}H_{16}S_2$, but that is not important since it is already a well-known fact. The author was especially interested in the soft rubber region, so that most of the concentrations selected were in that zone. It is quite obvious from looking at the curve that there is not the slightest trace of formation of any chemical compounds until the 32% compound is reached. We can also see that the amount of sulfur taken up is practically directly proportional to its concentration.

When you come to think of it, it is quite possible that all the values in the above experiment represent a condition of a false and not a true equilibrium. Spence and Young[24] have shown that, on heating a 10% sulfur-rubber mixture for 30 hours at 135° C., there was no free sulfur left. It stands to reason, therefore, when a strip of rubber is immersed in a dilute sulfur solution of butyl alcohol and heated, that all the sulfur should be taken up completely by the rubber if the process of vulcanization be prolonged for a sufficiently long period of time. At vulcanization temperatures sulfur is quite soluble in rubber. As the sulfur combines with the rubber, more of it should naturally diffuse into the rubber from the butyl alcohol. It is also known that sulfur is more soluble as the coefficient of vulcanization is increased. This, likewise, should increase the rate of sulfur depletion. Theoretically this transfer of sulfur should go on until all the sulfur is gone unless enough sulfur is present to produce the upper limit hard rubber compound $C_{10}H_{16}S_2$.

To counteract the above efforts for complete elimination of the sulfur we have the fact that, with progressive vulcanization, the diffusion of the sulfur becomes slower until it finally becomes zero with coefficients of vulcanization beyond 7 per cent. The temperature at which the experiments were conducted (117° C.) is a very low temperature for proper vulcanization so that the reaction proceeded at an unusually slow rate. The net result of the above opposing actions would be to create a static condition which might be classified as a false equilibrium.

[24] *Kolloid-Z.*, **11**, 28 (1912).

Conclusion

After subjecting all the possible theoretical assumptions for a theory of vulcanization to experimental verification, we are now ready to correlate our results and to eliminate those considerations which experiments have shown to be unwarranted.

In the first place, it has been shown, quite obviously, that the process of vulcanization cannot be interpreted as a solid solution of the sulfur in the rubber.

The discussion in the introduction has discredited quite effectively the hypothesis of pure adsorption. The assumption of a chemical compound linked together with an adsorption process is a much more reasonable one. However, when this theory was subjected to proper experimental verification, it likewise failed. The natural inference, on the basis of this theory, was that it should be possible to synthesize a vulcanized product from mixtures of raw and vulcanized rubber. The reverse of this, the ability to detect heterogeneity by fraction peptization, should likewise naturally follow. Both these deductions failed to materialize experimentally. Hence, we cannot lay much faith in a theory of this type.

It is not necessary to mention the objections to the supposition that the nature of the rubber is changed during vulcanization, since they have been explained in the introduction.

We cannot receive much comfort from the experiments on the equilibrium relations since we are not absolutely certain that the values obtained are representative of true equilibrium. Nevertheless, the curve obtained is practically a straight line, without any intimation of the possible existence of any compounds with a sulfur content of less than 32 per cent. If there did exist some compounds, let us say at 1 or 2 per cent intervals, the author thinks it quite safe to assume that they would have been easily discernible by the work performed in this experiment.

Of course, the experiment on the existence of a giant molecule showed clearly that we cannot consider a piece of rubber as one single molecule. Likewise the experiments on fractional peptization have shown that homogeneity persists even in vulcanizates with as low a coefficient of vulcanization as 0.1 per cent. This would naturally imply that if chemical combination were assumed, a molecular weight of close to 32,000 would be the smallest that we could ascribe to rubber for the purpose of forming the compound $(C_5H_8)_{470}S$, containing 0.1% sulfur. Work along this line has been done, showing that it is possible, by fractional peptization, to separate a mixture of two different vulcanizates in which the coefficients of vulcanization differed by 0.2 per cent.

Now that we have considered all phases of the subject we are in a better position to offer an explanation of the vulcanizing process. All the work done so far proves unquestionably that the nature of the union between the rubber and sulfur is a chemical one. Weber's theory thus far has been the most satisfactory. Of course, the very nature of his theory is such that one cannot subject it to experimental verification. He assumes that the series of compounds formed are so similar to each other that it is impossible to separate them. Nevertheless his theory explains things beautifully. It accounts for the gradual change in physical properties with progressive vulcanization. Although the best in its time, it needs only a very slight modification to enable it to account for all the facts known today. We must be able to account for the fact that it is possible, by the use of ultra-accelerators, to vulcanize rubber with coefficients of vulcanization much lower than Weber had assumed for initial compound containing 2.29% sulfur. Now that we have discarded the initial compound of Weber's series, it is necessary to find another one that is justifiable by some experimental proof in heading an analogous series of compounds. In selecting the proper size for the rubber molecule, it has already been shown that the giant molecule is too big and that homogeneity persisted with vulcanizates

containing as low as 0.1% of sulfur. Of course, experiments might have shown that homogeneity perisisted even with vulcanizates containing less sulfur, but then it would be impossible to check this experimentally, since the analytical chemistry is not that accurate. Therefore, it is conservative to postulate that the molecular weight of rubber is at least 32,000 in order to account for the initial compound of a series that would extend up to a compound containing 32 per cent sulfur. This initial compound must account for a sulfur content of 0.1 per cent. Hence its formula would be about $(C_5H_8)_{470}S$.

In recapitulation, one might say without hesitation that the essential ideas embodied in Weber's theory are still effective in offering the best explanation of the vulcanization process. The introduction of a new series of compounds starting with a sulfur composition of 0.1 per cent increases the value of n in the general formula $(C_5H_8)_nS$, so that the compounds formed are much more closely related to each other in physical properties than they were in Weber's original series. Thus the very idea which he tried to stress in postulating his series of compounds becomes much more emphatic when the series is changed to account for new facts.

[Paul Bary has written a critical review of this paper of Bacon, which need not be reproduced in detail, but from the last part of which the following translation may be of interest. For the complete paper of Bary, see *Rev. gén. caoutchouc*, Vol. 5, No. 45, pp. 3–7, Oct., 1928.—EDITOR.]

Discussion of Experiments upon Giant Molecules.—By the term giant molecules Bacon refers to products of polymerization of the parent C_5H_8 or $C_{10}H_{16}$ molecule. To many chemists, polymerization explains satisfactorily most of the physical and chemical properties of rubber, though there has been no confirmation. This polymerization, which varies with the temperature and mastication, may become fairly great in rubber kept at rest at a low temperature, as a result of which giant molecules are formed. When these molecules are brought to a relatively high temperature, as in vulcanization, the substance formed from them becomes plastic and viscous, a change which is due to a reduction in the degree of polymerization. Therefore if the giant molecules are originally present in the rubber, they are reduced by vulcanization and the properties of the mixture are changed.

Moreover tests made by peptization prove nothing concerning the size of the original molecules. It has been shown by the author[25] that the swelling of lyophilic substances, particularly rubber, by solvents brings about the beginning of depolymerization and solvation. When this depolymerization has gone far enough the molecules become so small that they are dispersed in the swelling agent and peptization begins.

If one agrees with Weber and d'Axelrod[26] that during vulcanization the molecules of combined sulfur are interposed among the more or less long molecules of rubber and that the new properties of the vulcanizate are due to the greater strength of the sulfur bonds which replace those of the simply polymerized rubber, one will readily understand that the giant molecules, which are weakly sulfurated, rupture in swelling, give products which can be peptized.

The experiments on peptization are therefore not conclusive for the rejection of the theory of giant molecules, since, if these molecules exist, swelling and peptization can take place only by their decomposition.

Vulcanization at Low Temperature.—Vulcanization by very small proportions of sulfur in the presence of ultra-rapid accelerators is an important point which remains unexplained by Bacon. Some other difficulties have been left unmentioned, particularly the question of the degree of polymerization of raw and of vulcanized

[25] *Rev. gén. colloides*, **4**, 322 (1926); *Rev. gén. caoutchouc*, **3**, No. 26, 5 (1926).

[26] *Gummi-Ztg.*, **24**, 352 (1909).

rubber, as well as the continuity in the variation of the physical and mechanical properties of the compounds $(C_5H_8)_n$ and $(C_5H_8)_nS$. These latter difficulties are easily overcome if one concedes, as the author has shown,[27] that unvulcanized rubber is a complex system of molecules of different degrees of polymerization and that the coefficient of polymerization n is only a statistical mean. There is now evidence that it contains 2 kinds of polymers, α and β, of very different coefficients n,[28] transformable from one to the other by heating or cooling, stretching or rest, mechanical fracture, solution, light, etc. The various experiments carried out to demonstrate these facts now leave no doubt as to the reality of these transformations.[29] Since the higher the temperature, the smaller is the mean degree of polymerization, it is evident that vulcanization at low temperature does not require so much sulfur as at the customary temperatures of 140° or 145° C. In the same way, vulcanization by sulfur chloride is not usually carried so far as that with sulfur. Then again saturation of the available double bonds at a temperature sufficient for vulcanization does not guarantee resistance of the rubber to the action of heat or repeated mechanical stresses. In fact, if the temperature is raised above that of vulcanization, there is a new depolymerization and the rubber becomes undercured. It is probable that this effect could be readily observed in the vulcanizates containing only 0.1% sulfur mentioned by Bacon, even while admitting, as probably must be done, that the accelerator used acts on the rubber in a similar manner to sulfur, as Ostromuislenskii[30] has shown for a large number of organic substances.

General Conclusions.—Naturally it could not be expected that a work, even as important as that under discussion, would completely satisfy all opinions and objections concerning the complicated problem of vulcanization. The chief point for which there is evidence is that the sulfuration of rubber is a chemical phenomenon, and that in this reaction adsorption plays only a secondary part, or perhaps no part at all if by adsorption is meant a solution of sulfur in rubber. The work of Bacon devotes some attention to unworkable theories based on the existence of two distinct phases in vulcanized rubber, one the sulfurated compound, the other pure rubber. It is only to be regretted that the experiments do not take into account the more modern theories which have been developed and which are based on colloidal properties. It is interesting to note that the observations are not at variance with these more recent theories.

[27] *Rev. gén. caoutchouc*, **2**, No. 20, 5 (1926); **2**, No. 21, 3 (1926).

[28] Bary, *Le Caoutchouc*, Dunod **1923**, 45.

[29] *Kolloidchem. Beihefte*, **22**, 63; **23**, 64 (1926). *Compt. rend.*, **184**, 947 (1927). *Rev. gén. caoutchouc*, **4**, No. 31, 3 (1927); **5**, No. 42, 3 (1928).

[30] *J. Russ. Phys.-Chem. Soc.*, **47**, 1467, 1885, 1898, 1904 (1915).

[Translated by J. P. Fahy from Kautschuk, Vol. 4, No. 9, pages 185–190, September, 1928.]

The Isomerization of Rubber to Cyclorubber under the Influence of High Tension Alternating Currents

Guido Fromandi

Chemical transformations by means of high tension alternating currents, accompanied by the activation of oxygen were investigated extensively toward the end of the last century by de Hemptinne,[1] who studied the behavior of a large number of chemical substances and systems under the influence of these discharges. These transformations are in general characterized by the fact that the discharge causes deep seated changes in the molecular structure of the substances, principally organic, on which it acts. The chemistry of some, indeed most, of the reactions produced by the silent electric discharge in liquid and solid systems has never been definitely explained, particularly when these reactions are accompanied by a complete destruction of the molecule. In the so-called "Voltol" oil process, the oil becomes more viscous when treated by the silent discharge and becomes a valuable lubricant, well known in the automotive market today. This product led to a thorough knowledge of the process and to a confirmation of Nernst's theory, according to which the increase in viscosity is due to a displacement of the intramolecular bonds caused by the impact of ions and electrons, resulting in the formation of polymerization products of high molecular weight. The discharge is produced in a rarified atmosphere of hydrogen, and due to the alternating field the ions and electrons in the gaseous layer undergo such acceleration that they increase markedly in numbers by impact. Because of their great kinetic energy the effect on the liquid molecules is exceptionally violent. The molecules split off hydrogen, which, because of its atomic, highly active form immediately becomes attached to the unsaturated bonds, forming saturated compounds. This is true of saturated as well as unsaturated compounds used as the substances to be treated, the mechanism of the reaction being characterized by the following general equation:

$$C_nH_{2n+2} + C_mH_{2m+2} = H_2 + C_{n+m}H_{2(n+m)+2}$$

In view of this work, natural rubber purified by Pummerer's method[2] and synthetic rubber (both the "normal isoprene rubber" and the "sodium rubber") were subjected to this electrical treatment in the hope of obtaining changes of a chemical and mechano-structural nature, and then explaining the phenomena not only on the basis of the generally accepted theory of the structure of rubber, but also from a physico-chemical point of view.

Reactions produced in most substances by high tension currents are very complex, making any simple explanation out of the question, so that there was no definite idea as to how rubber would behave. However, it is known that the extent of polymerization of synthetic rubbber is considerably different from that of natural

[1] For a comprehensive bibliography up to 1925 see Tiede, "Umsetzungen mittels stiller elektrischer Entladungen" (Stähler, *Handbuch anorg. Arbeitsmethode*, **2**, 1560–85 (1925).

[2] *Ber.*, **60**, 2148 (1927).

rubber (according to Hock[3] it is "more fluid"), and therefore it was possible that synthetic rubber might be polymerized by the silent discharge so that its properties would become more nearly like those of natural rubber.

The electrical apparatus consisted essentially of an alternating current machine with a high periodicity, the single-phase current being transformed by a small induction coil to the required tension of about 4500 volts.

At the beginning of the experiments the rotating Voltol tube of Hock[4] was used, which consists of two concentric tubes similar to a Siemens ozonizing tube. Later a modified form of the apparatus used by Becker[5] in his work "The Increase in the Viscosity of Oil by the Silent Discharge" was adopted. The apparatus works on the the mammoth pump principle. After placing the material in the reaction chamber, current of gas is introduced at a pressure of 18–19 mm. mercury, which together with the discharge causes considerable foaming. The material is circulated continuously, so that an intensive electric treatment is possible.

By the method employed, the dissolved rubber is first subjected to the effects of the discharge. Absolute freedom of the solvent from oxygen, whose molecules are dissociated by the discharge to oxygen atoms or to ozone, which form oxidation products, complete neutrality toward hydrogen, and finally a favorable point in the vapor pressure curve were determinant factors in the resulting reactions. Decalin (decahydronaphthalene) was chosen as the most suitable solvent, as it satisfied very well these conditions.

Purified hydrogen was used exclusively for the gaseous atmosphere to avoid complicated specific chemical reactions which the behavior of decalin alone, when subjected to a discharge in oxygen or nitrogen, clearly showed would occur. Moreover, hydrogen played an important part because of its conductivity, the ease of separation of electrons from the molecule, and especially because of its influence on the chemical effect of the silent discharge.

The course of the experiments made it necessary to learn something first concerning the behavior of decalin—merely as a solvent—when subjected to the high tension alternating current. After an eight-hour treatment decalin showed an increase in viscosity due to strong polymerization, and then passed over to a hard powder, whose average molecular weight was about three times that of the original decalin.

In order to obtain the rubber from its solution in decalin after the electrical treatment without the reaction products of the decalin which would be precipitated at the same time on adding acetone, the effect of the glow discharge on the rubber dissolved in decalin was determined in the following way: After about an hour's treatment, while the decalin was still neutral to acetone, the rubber was precipitated and then dissolved in fresh decalin, so that the changes in the solvent caused by the discharge were completely avoided.

By varying the duration of treatment, stages of the reaction were obtained, little change occurring after an eight-hour treatment. This suggests that a certain equilibrium occurs which, however, is not thermodynamic—but rather a condition which is finally stable and which is in general a function of such factors as tension, temperature, pressure, etc.

The effect of the electric discharge on rubber produced essential changes in its chemical and physical properties, which were determined by a series of experiments, and which are shown by the following graphs.

Thus in Fig. 1 natural rubber shows a relatively marked decrease in viscosity de-

[3] *Kautschuk*, **1**, 65 (1925).
[4] *Z. Elektrochem.*, **29**, 113 (1923).
[5] *Wiss. Veröffentlich. Siemens-Konzern*, **5**, 160 (1926).

pending on the length of treatment, though the elementary composition remains unchanged throughout all stages of polymerization. Furthermore with increasing treatment there is a progressive decrease in the iodine number and therefore in the degree of unsaturation until a value is obtained that corresponds to the disappearance of about two-thirds of the double bonds originally present. There is finally a constant decrease in the softening temperature, and in the average molecular weight as determined by measuring the depression of the freezing point of menthol according to Pummerer's method.[6] The intermediate products as well as the hard yellowish white powder obtained after eight hours' treatment are essentially different from the original rubber in their properties, such as their behavior toward sulphur chloride, and their rate of solution in benzene, petroleum ether, carbon disulfide, etc.

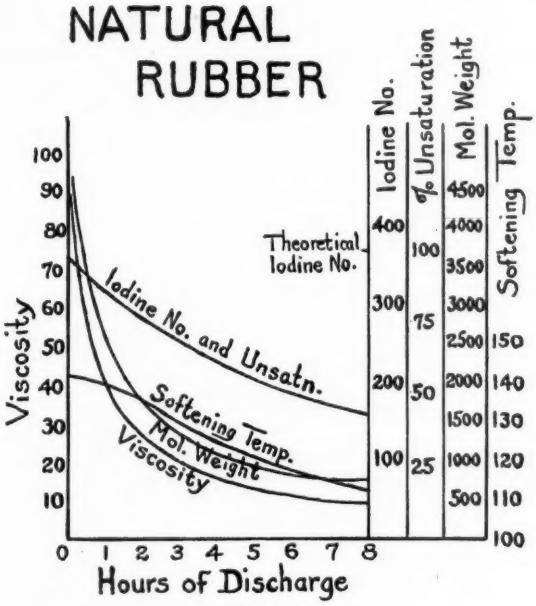


Figure 1

Similar conclusions result from a comparison of the products obtained by electric discharges with the cyclorubbers prepared by Staudinger[7] in a purely chemical way, as for example by treating hydrogen halides of rubber with zinc dust and acetic acid in high boiling solvents, by heating at high temperatures, by distillation in two steps,[8] etc. The effect of high tension alternating currents on rubber is therefore a process which consists of an isomerization of rubber in stages to mono- and polycyclorubber, the mechanism of the reaction being interpreted in the following way: The impact of the ions and electrons due to the alternating discharge causes a loosening or displacement of the double bonds of the rubber molecules, permitting the formation of a ring compound. In contrast to the formation of Voltol oil mentioned above, where the alternating field causes a polymerization of the oil molecules, here we have a cyclicization process, which probably consists of a dis-

[6] *Ber.*, **60**, 2167 (1927).
[7] *Kautschuk*, **1** (1925); Geiger, Diss., Zürich, 1926.
[8] *Kautschuk*, **4**, 146 (1928).

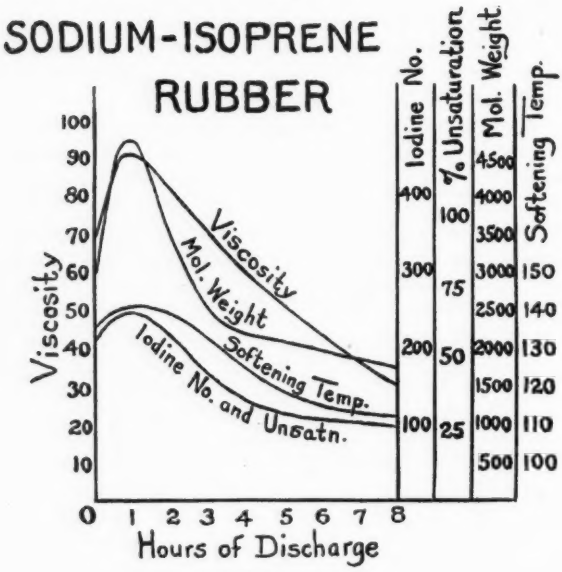


Figure 2

placement of the double bonds in four rings, where, according to the Staudinger theory, free end valences as well as the double bonds take part in the cyclicization.

Now, while the alternating discharges caused in natural rubber a cyclicization at each step, sodium-rubber (Fig. 2) and normal isoprene-rubber (Fig. 3) at first

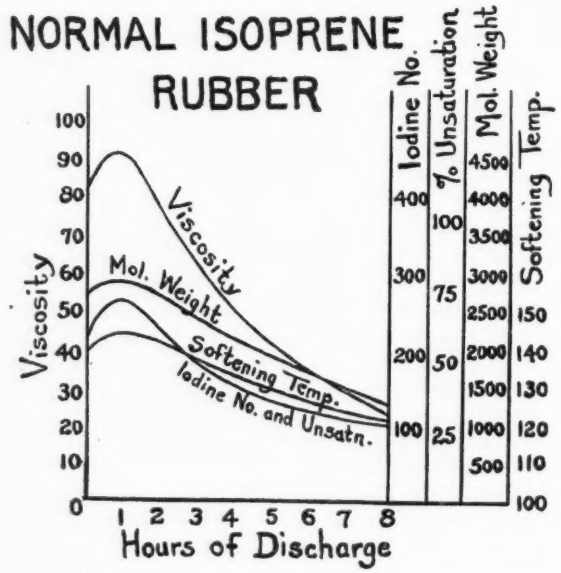


Figure 3

showed an increase in the relative viscosity, iodine number, molecular weight and softening temperature, thus differing in behavior from natural rubber.

After a treatment of about an hour, both types of synthetic rubber assume the same appearance as natural rubber, and finally a powdery product is obtained, which has the same elementary composition as the original material. The relatively low iodine number of 206–209 (theoretical 372.8) and the viscosity indicate that the distinction between synthetic and natural rubber is due to a difference not only in the colloidal structure but in the chemical structure. This offers support to Staudinger's theory, according to which synthetic rubber has a cyclic structure, which in turn may explain its lesser nerve and ability to vulcanize and its poor mechanical properties. At the beginning of the discharge synthetic rubber approaches natural rubber in chemical structure, and the whole course of the curve indicates that the change is also of a colloid-chemical character. Synthetic rubber which has received a one hour treatment yields a "synthetic latex" upon the addition of acetone, which superficially resembles the natural product in every way. (Wo Ostwald[9] has already pointed out the influence that a synthetic latex has upon the physical structure of the rubber precipitated from it.)

The effect of the silent electric discharge on synthetic rubber consists therefore first of all of a polymerization, preceded by an opening of the ring compound, followed, on further treatment, by the formation of a more stable cyclic compound, as in the case of natural rubber, until four-fifths of the double bonds originally present have disappeared. It appears then that electrical treatment causes ring compounds to open as well as to close, and it is a question of the rate of reaction which tendency predominates. Hence, with suitable electric and thermal conditions, it is possible to stop the cyclicization at any point, and even to reverse the process, so that it should eventually be possible to make synthetic rubber with properties closely resembling those of natural rubber. Experiments in this direction are in progress.

[A theoretical discussion dealing with the relation of the results to the structure of rubber is omitted.]

[9] "Die Welt der vernachlässigten Dimensionen," p. 276. Dresden, 1927.

[Reprinted from Transactions of the Institution of the Rubber Industry,
Vol. 4, No. 3, pages 210–234. October, 1928.]

Methods of Determining Abrasion

With Particular Reference to the Relation between Road Performances and Laboratory Tests

L. J. Lambourn

Many previous papers have included descriptions of abrasion machines, but few have dealt particularly with the correlation of road performance and laboratory tests. It must be admitted in the first place that no abrasion machine, however good it may be, has yet been designed to replace road tests. None of the abrasion machines of the small laboratory type takes pattern into account, for example. Of course, there are one or two abrasion testing machines in which a complete tire is used, but they are not in favor, in view of the expense and time involved in obtaining results.

Variation in Relative Road Results.—Relative road results on tread wear may be considerably influenced by external factors such as speed, road surface, front or rear wheel service, tire design, etc. In view of this possible variation in relative wear, it is obviously necessary to eliminate as many of the causes as possible when comparing two tread compounds on the road. Probably the best way is to make a tire tread in two halves, *i. e.*, one-half of the tread circumference of one mixing and the other half of another mixing; these halves joined together before curing form a perfectly sound tire. If the compounds cure at different rates, and this method cannot be employed, the best plan is to make a pair of tires of the same design and fit them, say, to the rear wheels of a car, and interchange them from near to off wheels every 500 miles.

Even so, it is useless to rely on one or two tires to give the relative road results on tread wear; at least four distinct comparisons are necessary. It is not uncommon for the relative abrasion of two mixings to change during the actual course of the road test.

The Effect of Front and Rear Wheels on Relative Wear.—It is quite certain that tire treads become more nearly alike, with regard to wear, on rear wheels than on front wheels, *i. e.*, the difference in abrasion is more pronounced on front wheels. The difference is due to the different behavior of front and rear wheels. The former are merely rolling along and wear out because of steering vibration, camber, toe-in, braking and "pattern slip." On the other hand, rear wheels are rolling in a straight path and transmitting the power, and this masks the effect of "pattern slip."

In order to arrive at an average relative road result, therefore, it is necessary to make both front and rear wheel tests. The front wheel test will tend to magnify the difference between two compounds, for instance, and the rear wheel test will tend to minimize the difference.

Facts to Be Considered in Designing an Abrasion Machine.—The variations likely to occur in road performance tests and the precautions necessary to obtain reliable relative figures have been noted, and it is now possible to consider the requirements of an abrasion machine. What is required by the tire manufacturer, and in particular by the man responsible for the tread compounding, is a rapid and consistent test which will give relative abrasion figures for conditions representing average

service. The efficiency of the test will depend upon its reliability in giving the same abrasive index for a given compound day after day, month after month.

The abrasion index, of course, must be in arbitrary units. In nearly all abrasion tests, the volume or percentage volume of rubber worn away is measured, and all results are expressed relatively, in terms of a standard mixing, whose average road performance is known.

With regard to the degree of accuracy required in the laboratory machine, results correct to within 5 per cent should be obtained. Greater accuracy is not necessary in view of the road variations, and in any case would be very difficult to obtain.

Although a laboratory machine cannot be expected to imitate road testing, with regard to actual rate of wear, since testing would be far too slow, it should follow the general principles of tire wear. For instance, it is advisable to have an arrangement whereby the rubber has a chance to recover and to cool after it has been subjected to stress and abrasion. The period of distress and the interval between successive stresses should, if possible, be of the same order as in practice.

Further, a nearer approach to service conditions is obtained if the power is transmitted through the rubber, as in a rear wheel tire. Probably the most convenient arrangement for complying with all these conditions is to have the test sample in the form of a wheel or disk, so that it rotates against an abrasive surface.

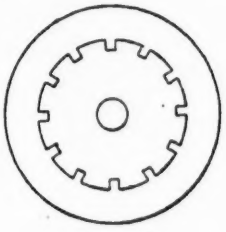


Fig. 1

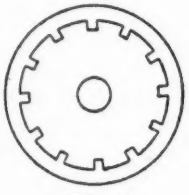


Fig. 2A

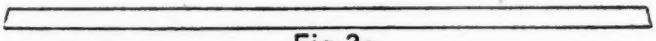


Fig. 2B

The mechanism of wearing away rubber on different abrasion machines varies considerably. The abrasion on some machines is largely determined by a tearing action; on others the tearing action is not nearly so pronounced as a cutting action. A tire tread has to withstand both cutting and tearing, and therefore the machine which will give the best relative results for tread stocks must give due emphasis to both of these actions.

The amount worn away when a piece of rubber is moved against an abrasive surface depends on the nature of that surface, on the intensity of pressure between the rubber and the abrasive, and on the amount of slippage between the rubber and the abrasive.

This applies to a tire on the road in the same way as it applies to a laboratory sample rotating on an abrasive disk. For an abrasion machine to be really useful, both the pressure intensity and the degree of "slip" must be controllable.

A description will follow of a machine which embodies the principles outlined above and which was evolved after many attempts with other simpler types of machine had failed to give the desired result. In this machine the amount of slip

between the rubber and the abrasive is absolutely controllable, and can be varied with ease, during the test, if required.

Description of "Controllable Slip" Abrasion Machine (British Patent, No. 282,-

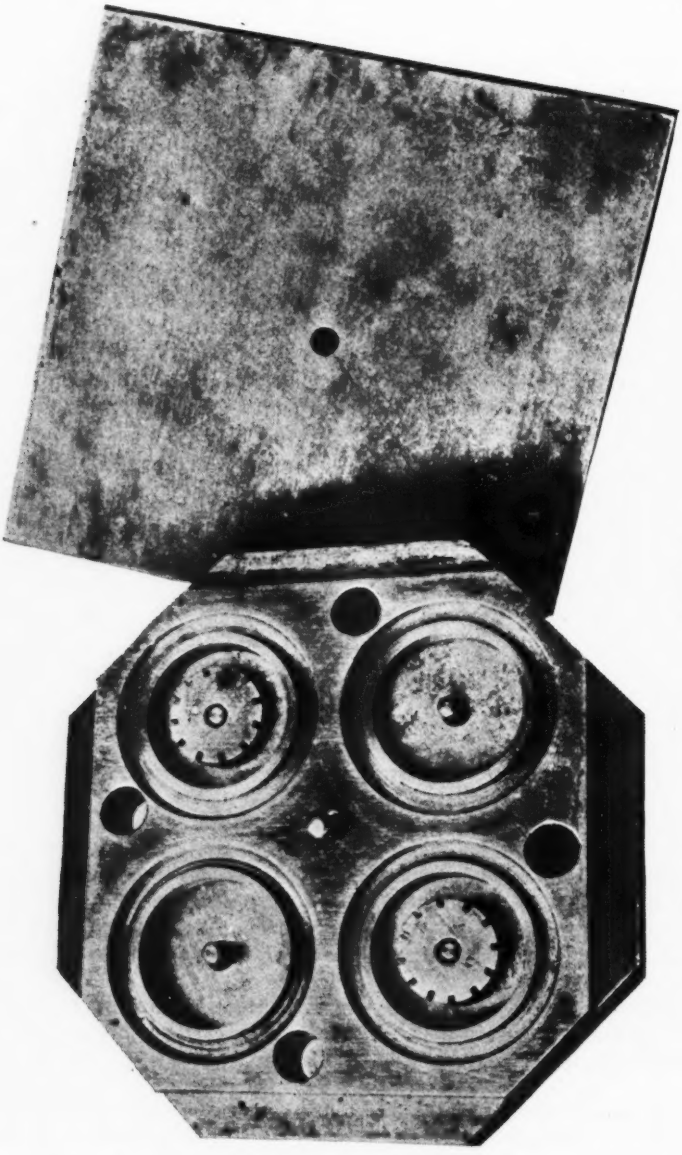


Figure 3

131).—A small rubber test wheel, about 4.3 cm. in diameter and 1 cm. thick, is subjected to a driving action under load over an abrasive track.

There is a "cornering" effect due to the circular path of contact between the

rubber wheel and the track. The combined effect is to give an accelerated abrasion so that results may be obtained rapidly. The volume of rubber abraded under known conditions during a given period is determined. This is obtained from the loss in weight and the specific gravity of the rubber under test.

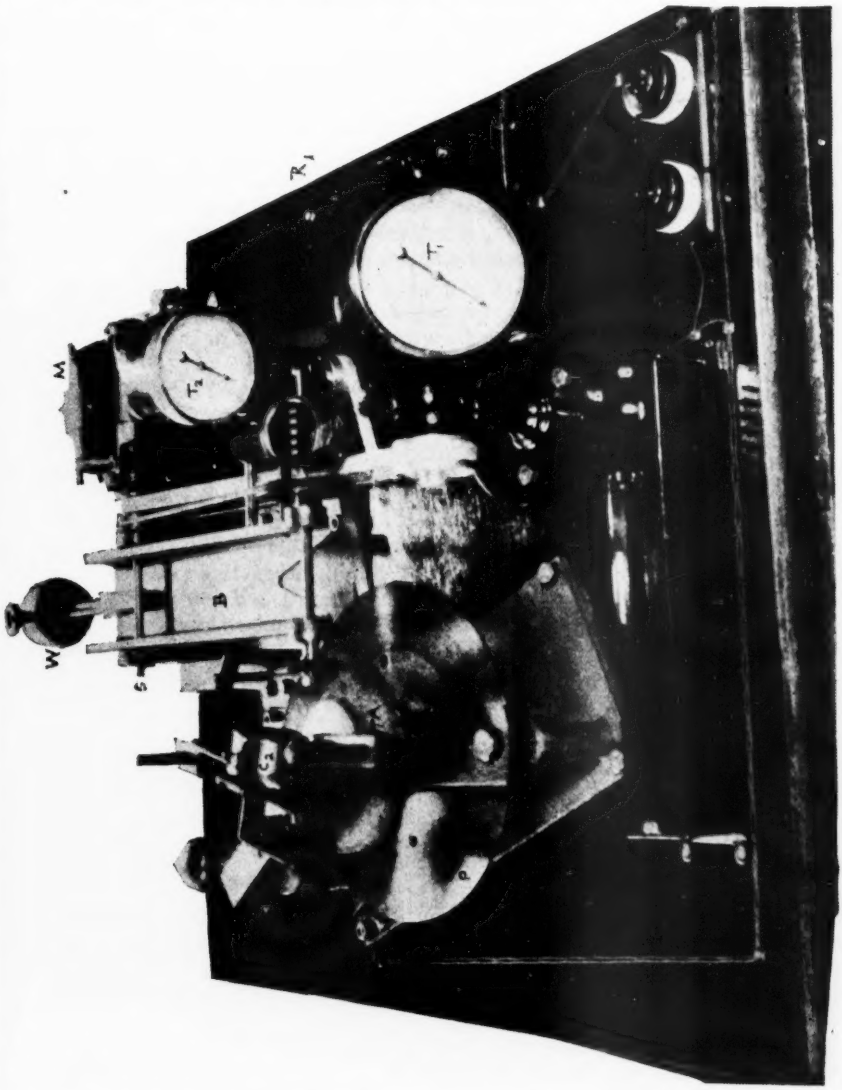


Figure 4

The test wheel may be made either by moulding the rubber on a metal center, as in Figure 1, or by solutioning round a smaller moulded center (Fig. 2a) a strip, (Fig. 2b), cut from a tire tread, for example. A photograph of the four-cavity mould is shown in Figure 3. The arrangement for testing is shown in the next photograph, Figure 4.

The test wheel is securely mounted on the front spindle of the bracket *B*, by means of a washer slightly smaller than the metal center, and a nut, so that there is no possibility of squeezing the rubber. The bracket which carries the test wheel is pivoted on the rear spindle S and is provided with a counter-balance weight W, so that any desired load can be applied to the test wheel.

The test wheel is driven at a speed of 600 revolutions per minute, by means of a motor M; the speed being indicated by the tachometer T_1, and controlled by a rheostat R, across the armature of the motor. The drive is transmitted through the rubber to the abrasive wheel, which rotates at a speed recorded by the tachometer T_2. The number of revolutions of both test wheel and abrasive wheel can be read off on the counters C_1 and C_2, respectively.

The abrasive wheel is 7 in. in diameter, and the actual diameter of the track is 6 in. (15.24 cm.). The diameter of the test wheel is 4.3 cm. as stated. If there were no slip between the rubber and the abrasive wheels, the ratio of the speeds would be in the inverse ratio of their diameters.

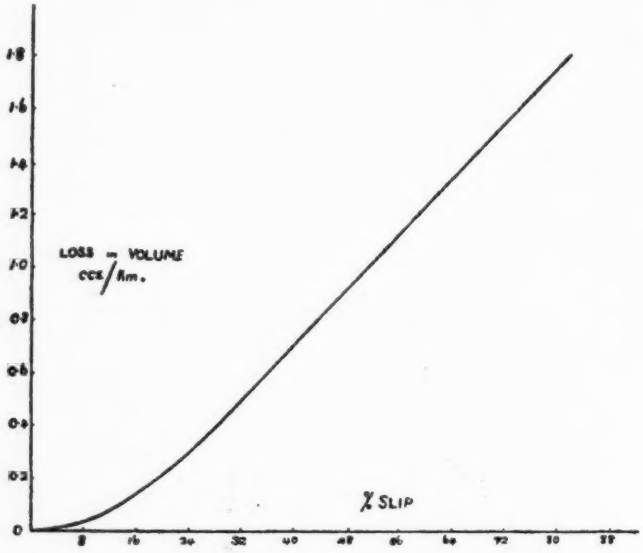


Figure 5—Abrasion-Slip Curve

If the rubber test wheel is made to slip with respect to the abrasive wheel, the amount of slip can be readily determined from its actual speed and the calculated speed; in other words, from the number of revolutions it actually makes in a given time and the number of revolutions calculated from the respective diameters. (See Appendix 1.)

The slip is produced by means of an eddy current brake. Eddy currents are set up in the copper plate P, due to its motion between the poles of the electromagnet when a current is passed through the latter. The copper plate, being coaxial with the abrasive wheel, acts as a brake, thereby causing slip between the rubber and the abrasive. By varying the current in the electromagnet, the amount of slip can be varied at will, and by using both tachometers in conjunction with rheostats, any desired amount of slip may be maintained.

The surface of the abrasive wheel is kept clean and free from particles of abraded

rubber by means of a rotary wire brush, arranged obliquely to the track, and an air suction pipe, A.

An ammeter may be included in the electromagnet circuit (it is not shown in the photograph).

It is obvious that the amount of slip will have a considerable influence on the volume of rubber worn away, other conditions remaining the same. A typical curve showing the relation between abrasion (volume worn) and amount of slip is shown in Figure 5. Approximately the rate of wear increases with the square of the slippage, up to values of 25 per cent slip; above that value the relation is approximately linear.

It has been established that the best conditions of working the machine are those of constant slip. That is to say, in order to obtain results on a wide range of compounds which agree with average road results, it is best to work with the same amount of slip between test wheel and abrasive wheel for all compounds.

The advantages of testing at constant slip are (1) standardized conditions for routine testing and (2) elimination of errors due to friction in the bearings. For instance, if the friction in the bearing increases, thereby putting a mechanical drag on the abrasive wheel, this is compensated for by using a little less electromagnetic drag.

Calibration of the "Controllable Slip" Machine.—The original machine of this type was calibrated by taking several tread compounds with widely different abrasive qualities and having a large number of tires made up with "half-and-half" treads, as described at the commencement. The tires were run on cars all over the country. By this means the average road performance of the various compounds was obtained and could be expressed relative to a standard compound.

Samples of the actual treads, which were extruded for these tires, were kept in the laboratory and moulded in the form of test wheels.

These were tested on the machine, each at a range of "slips," so that an "abrasion-slip" curve could be drawn of a type similar to that in Figure 5. It was found that the best working figure for all the compounds was 16 per cent slip, and the table below which gives the relative laboratory results and the road performance tests side by side, justifies this figure.

Laboratory Results.			Road Results.
Compound.	Actual.	Relative.	Relative.
A	0.18	100	100
B	0.25	139	130
C	0.27	150	142
D	0.36	200	225
E	0.17	95	93
F	0.21	117	117
G	0.165	92	92
H	0.37	206	215
J	0.18	100	100
K	0.12	67	82

The actual laboratory results are expressed as volume of rubber lost (in cc.) during a kilometer run of the test wheel on the abrasive wheel. This has been taken in preference to a fixed number of revolutions of the test wheel, because it allows for test wheels of different diameters. The average diameter during the test is used for purposes of calculation.

The other results are expressed as relative abrasion in terms of the standard compound A, *i.e.*, the higher numbers indicate inferior wear. Incidentally, the compound A does not contain ingredients liable to variation, such as reclaim.

The compounds A to K in the table embody quite a variety of compounding ingredients; some contain reclaim or crumb, some are accelerated and so on. The details and the relative merits of this series of compounds will not be discussed in this paper. It is sufficient to show the kind of agreement one gets between relative road and laboratory results on properly cured compounds when very varied ingredients are used.

It will be seen that in nine cases out of ten the agreement is very good; in the tenth case (K) the order of merit is right, although there is a difference in the magnitude of the two results. Many other compounds have been tested in this way. For example, the test has been applied to a motorcycle and cycle treads and excellent agreement between road and laboratory results has been obtained.

Magnitude of the "Slip" and Its Effect on Abrasion.—It is not assumed that the driving slip of actual tires in service is 16 per cent or anything like that amount. On ordinary motor tires under average touring conditions, it is probably nearer 1 per cent; it may reach 4 per cent on steep hills, and probably much higher values in rapid acceleration.

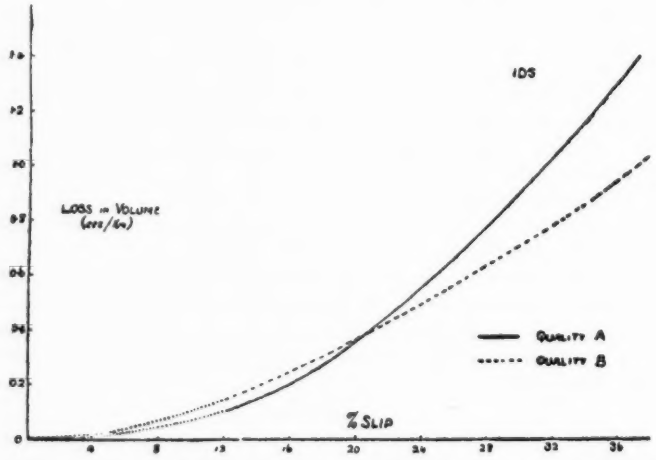


Figure 6—Effect of "Slip" on Abrasion Showing Changing Order of Two Different Compounds

In this connection, some experiments were carried out with a motorcycle combination, and the results obtained may perhaps be of interest at this juncture. The wheel slip was measured by recording the revolutions of the rear wheel (1) when it made only rolling contact with the road (by towing the motorcycle) and (2) when it was driven.

These were the results:

(1) Over a cross-country run of six miles with a maximum speed of 50–60 m.p.h., the total slip was only about $1^1/_2$ per cent.

(2) Over a rough road, a short run of one-third of a mile with a maximum speed of 62 m.p.h. gave a slip of $4^1/_2$ per cent.

(3) In a rapid "get-away" by fiercely engaging the clutch and accelerating to 30 or 40 m.p.h., in 140 yards, a slip of 16 per cent was obtained.

(4) In a similar "get-away" and measuring the slip over a distance of 32 yards, a figure of 48 per cent was reached and the amount of wear on the tire in this case was very heavy.

This is undoubtedly one of the causes of excessive wear on tires fitted to powerful motorcycles and cars, capable of high acceleration. It has already been indicated that rate of wear increases approximately as the square of the slippage between the rubber and the abrasive, so the disastrous effect on the tires of fierce use of the clutch will be readily appreciated.

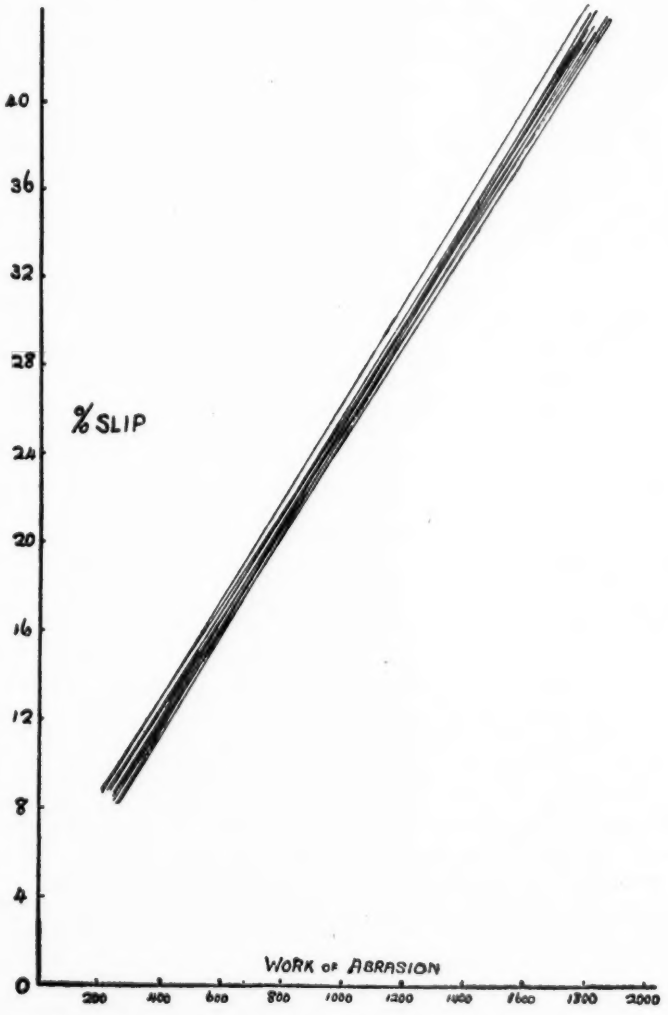


Figure 7—Relation between Work of Abrasion and Slip for Six Compounds

Apart from driving slip, there is the inevitable "pattern slip," which was referred to earlier in the paper.

The foregoing is rather a side track from the subject of abrasion machines, but it is well to realize what sort of variations in slippage may be obtained in practice.

To return to the question of testing at 16 per cent slip, in the laboratory. These conditions, whatever relation they have to those pertaining in practice, give the correct relative results for average service conditions for the majority of tread mixings, say nine out of every ten. With this amount of slip, a reliable figure for the volume of rubber worn away may be obtained in 15 minutes.

Changing the Order of Merit of Two Compounds.—An interesting feature of the relation between abrasion and slip is that the curves for two mixings may cross one another. (See Fig. 6.)

This means that a tread rubber which may be excellent for ordinary touring speeds (with low slip) may be useless for high speed work, *e.g.*, racing, with correspondingly higher slip. And conversely, the tread rubber suitable for race tires may not do so well under ordinary circumstances. This controllable slip machine, therefore, provides a ready means of testing rubber which is to be used for high speed work. It is a simple matter to do the abrasion tests with a higher degree of slip to determine which mixing shall be used; usually a hard rubber gives the best results under these conditions, it has a lower power consumption and consequently does not get so hot.

Work of Abrasion.—It was thought necessary at first to have an ammeter placed permanently in the electromagnet circuit to keep a check on the braking current. Measurement of this current makes possible a calculation of the work done on the test wheel during abrasion, or rather, a figure proportional to the amount of work done. It is shown in the Appendix that the work of abrasion is proportional to the amount of slip. Fig. 7 shows a series of curves which illustrate the relation between slip and work, for several different qualities of vastly different hardnesses.

It will be seen that these curves practically coincide: in fact the differences between them can be attributed to experimental error. (Calculation of the work of abrasion involves the square of the electromagnet current, so that any error in this current is doubled.) Hence testing at constant slip amounts to the same thing as testing at constant work.

Difficulties with Undercured Rubber.—In view of the fact that an abrasion index is a purely arbitrary number and is subject to considerable variations for many reasons, perhaps it is safe to say that an infallible abrasion machine is beyond human design. So it must not be imagined that this controllable slip machine is infallible. As already indicated, it probably gives a correct forecast of road performance in nine cases out of ten.

The case of compounds which are undercured calls for special comment. The machine in the form described gives lower abrasion losses for lower cures, or to put it in another way, the greater the degree of undercure, the greater the apparent abrasion resistance. It is generally supposed that a tire tread which is undercured will wear out faster than a properly cured tread. That this is not the case has been demonstrated in several road tests in which the service result has borne out the laboratory result. Of course, there are obvious reasons why it is inadvisable to have tire treads in an undercured condition. They would be more subject to cutting, for instance.

Such cases of agreement between road performance and laboratory tests occur when the degree of undercure is not too pronounced or when the particular road conditions are suitable, *e.g.*, smooth roads which are more or less dust free. If the rubber is so undercured as to be gummy, then difficulties arise. This "gumminess" may be due to some other cause such as an overdose of softeners in the compound, or in certain cases, overworking. The explanation of the low abrasion loss on the machine is fairly plain. The abraded rubber, instead of being sucked away in the form of fine powder, forms itself into rolls which adhere to the test wheel, causing

it to vibrate, with a tendency to less slip. Severe brushing during the test will not prevent this adhesion, and consequently the undercured or gummy rubber appears better than the optimum cured rubber.

No doubt the same thing would happen to a badly undercured tire tread in service, if the roads were dry and dust free. But the conditions are nearly always such that the adhesion is overcome between the small particles of abraded rubber and the tire and an increased amount of wear results.

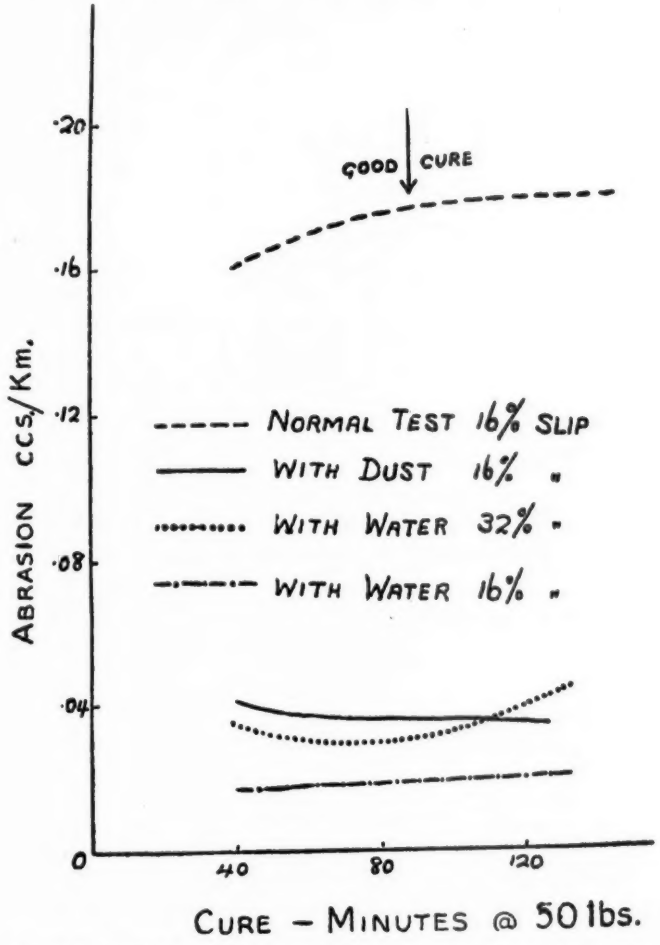


Figure 8—Variation of Abrasion with Cure Showing Effect of Dust and Water. Pneumatic Tread Compound

Such conditions as (*a*) a very rough road composed of sharp loose stones, or a road covered with fine dust, (*b*) severe driving, *e.g.*, sharp acceleration, with much wheel slip, (*c*) a wet road, seem likely to bring out the inferior wearing qualities of undercured rubber.

These conditions have been applied to the "controllable slip" machine with quite promising results. Taking them in the order given above.

(*a*) Fine dust, in the form of French chalk, has been applied to the test wheel or abrasive wheel. Testing under these conditions at 16 per cent slip has had the desired effect, and gives the highest abrasion resistance at the optimum cure. Moreover, it does not alter the relative abrasion of other properly cured qualities.

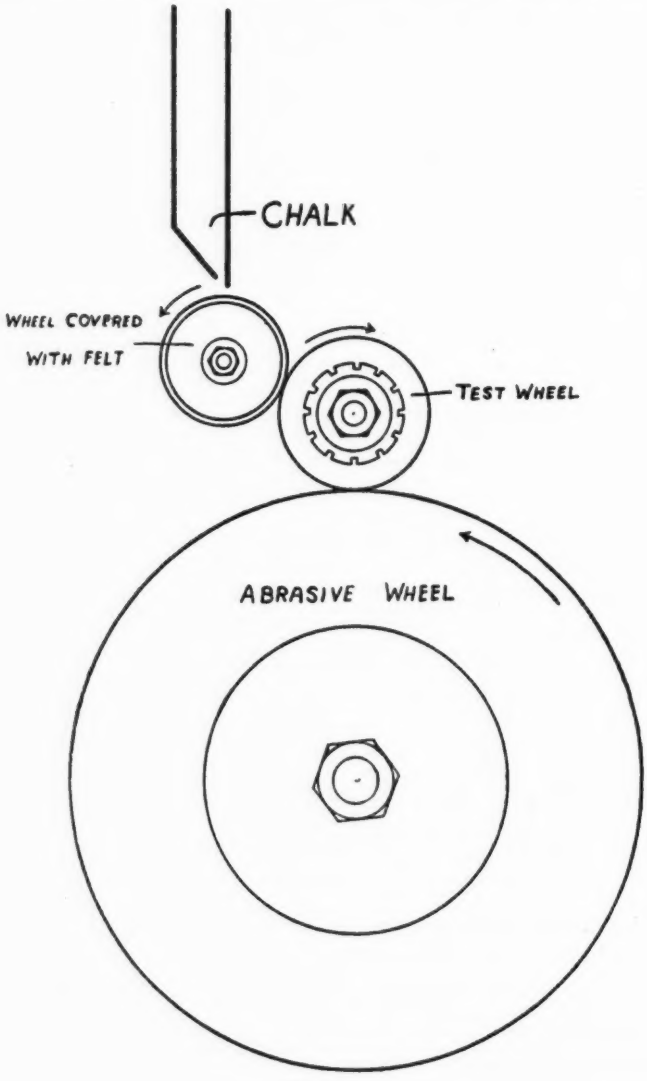


Figure 9

The disadvantage of the use of French chalk is that it slows down the rate of abrasion to about one-fifth of the normal rate, and this is too slow for testing on a routine scale. As French chalk acts as a lubricant it was thought that a gritty powder such as emery flour would be more useful. It certainly gives a faster rate of abrasion

than French chalk, but in experiments made up to the present the results have been rather inconsistent. The use of dust in overcoming the gumminess of undercured rubber is illustrated in Fig. 8, which shows a rate of cure test on a pneumatic tread stock at 16 per cent slip.

Much depends on the method of application of the powder. Consistent results were obtained with French chalk with the arrangement shown in Fig. 9.

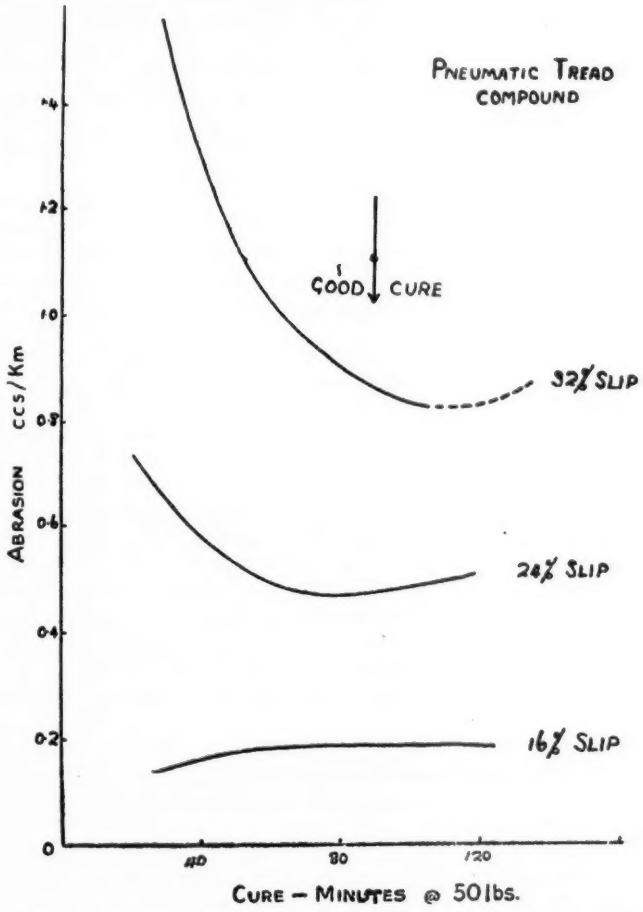


Figure 10—Effect of Cure on Abrasion at Various Degrees of Slip

For this and several other modifications of the standard test it will be noticed that the test wheel runs on the periphery of the abrasive wheel, which is mounted vertically. The arrangements for testing at any desired slippage are identical; the actual rate of wear is some 10 per cent slower, since there is no cornering action as in the machine shown in Fig. 1. The relative results are very similar, whichever arrangement is used.

When testing with chalk or any other powder, it is advisable to have the bearings of the abrasive wheel and copper disc well protected to avoid dryness and subsequent wear.

(*b*) The effect of severe driving has been obtained on the machine by doing tests at 24 per cent slip and at 32 per cent slip. Undercured rubber suffers the maximum abrasion with high slippage, as will be seen in Fig. 10, but these conditions unfortunately do not suit other mixings, as has already been indicated (in the section dealing with "Magnitude of slip and effect on abrasion.") Therefore this method of testing undercured rubber is not so good as the "dust" method described above.

(*c*) The application of water to the test wheel does not improve matters appreciably if the testing is done at 16 per cent slip, inasmuch as undercured rubber shows about the same abrasion resistance as properly cured rubber. In any case, it is impracticable for routine testing, since it slows down the rate of abrasion about ten times. If tests are carried out at 32 per cent slip, however, with the abrasive wheel running through water, an optimum abrasion resistance is obtained at the optimum cure, unless the rubber be scarcely cured at all.

Quite a number of abrasion machines have given false results on undercured gummy mixings. The New Jersey Zinc Company modified their machine to correct this fault. It will be remembered that they designed a cam arrangement to regularly raise and drop the holder carrying the test piece, simulating the jumping of a tire when accelerating or decelerating rapidly. This is equivalent to the condition (*b*) mentioned above.

Their results show a maximum resistance to abrasion at the optimum cure with this arrangement, whereas the original machine was very sensitive to cure and gave erroneous results.

Deterioration of Abrasive Wheels.—Routine abrasion testing, carried out on a continuous scale, causes deterioration of the surface of abrasive wheels. This is caused by the gradual smoothing or disintegration of the particles and not by clogging due to rubber dust, which may be effectively removed during testing.

There is no doubt that this deterioration occurs on all types of machines employing an abrasive wheel. The average period over which a wheel may be used on the controllable slip machine is two months for continuous testing of about forty hours per week. The wheel may then be reversed and used for another two months. In any case, variation in surface may be compensated for by testing daily a sample of a definite standard compound. When the supplies of the standard batch are almost exhausted, another batch must be mixed and overlapping tests made.

Several types of abrasive wheel have been used on this machine, including the following: (1) An aluminum oxide abrasive, of a proprietary make, soft grade and 46 grain. (2) Flint, medium grade and 40 grain. (3) Carborundum, soft to medium grade and 24 grain.

In general, it may be said that each of these gives approximately correct relative results, if tests are made at 16 per cent slip, but they are placed in order to merit in this respect. There are other factors which determine the type of wheel to use. The chief of these is the lasting properties of the wheel, to which reference has already been made; then there is the question of duplicating the wheel easily.

It is advisable not to use a wheel of a coarser grain than 24; otherwise the rubber is removed during the abrasion test in very much larger particles than in practice. This point can easily be verified by comparing the appearance of a worn tire tread with that of a sample of rubber after an abrasion test.

"Approximate Value" Abrasion Machines.—Quite apart from the precision machine for giving the best possible results in the comparison of rubber compounds, there is another type of abrasion machine which is very useful to the manufacturer, and this may be distinctively called the "approximate value" abrasion machine.

This type is particularly useful when the tire technologist wants to get a rough idea of the relative abrasion of two tires, without spoiling the tires for future service.

For instance suppose a statement is made that the mileage of two equally worn

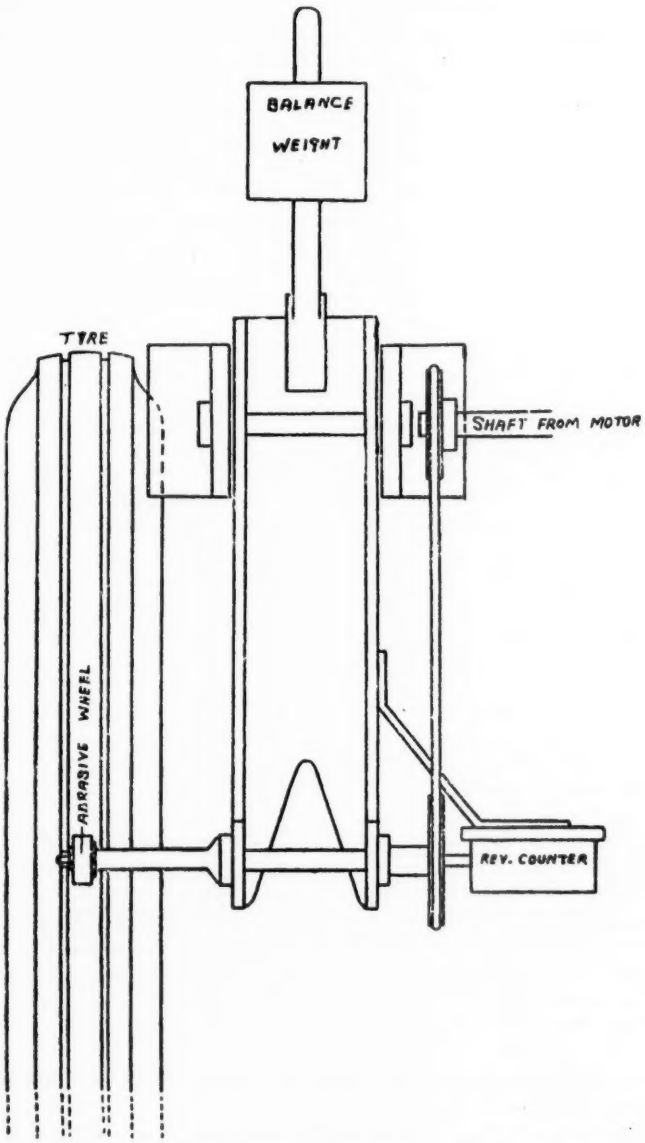


Figure 11—"Approximate Value" Abrasion Machine. Plan Type 1

tires of the same make differs by 100 per cent. The tires are wanted for further mileages, so that a rapid test, although only correct to 15 or 20 per cent, to prove

whether the discrepancy was due to rubber variation or to different service conditions, would be very useful. Of course, if the tires are not wanted for further mileage, an accurate comparison can be made by cutting strips from the tire treads and testing them as described earlier in the paper.

There are obvious difficulties in using these approximate value machines; the amount of rubber taken from the tread must of necessity be quite small. The

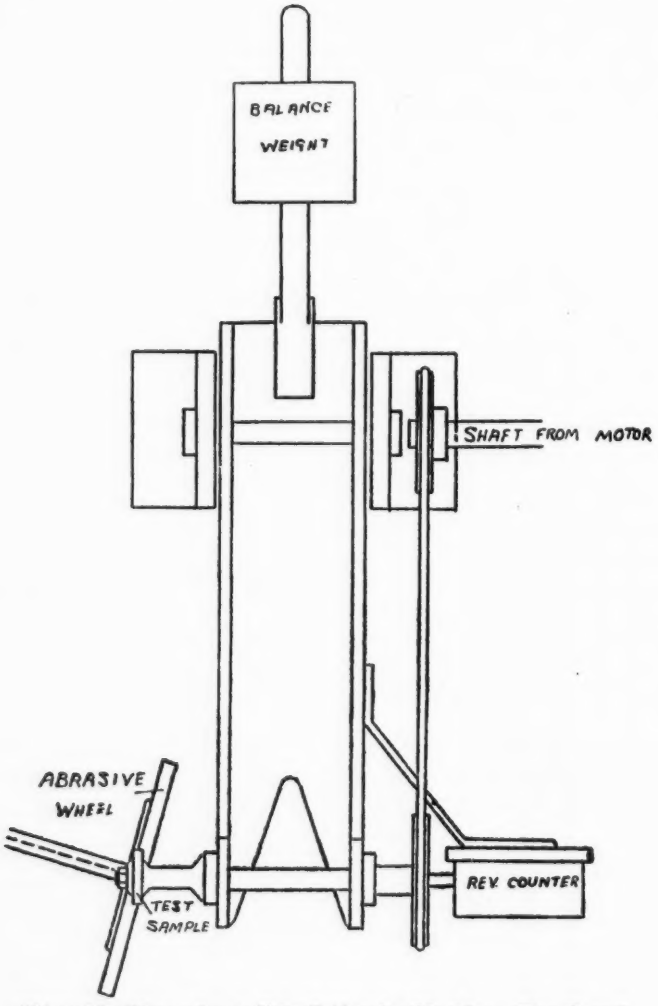


Figure 12—"Approximate Value" Abrasion Machine. Plan Type 2

following two methods, however, have been found fairly successful and give a degree of accuracy of 15 to 20 per cent.

(1) A small abrasive wheel (say two inches in diameter) is pressed with a fixed load against a point on the tread of a tire which is rigidly held. This small wheel is driven by a motor; the drive and the loading arrangements are conveniently

obtained by the method previously described. The wheel cuts a groove into the stud or bar of the tire tread; this groove may be quite small and shallow and the test be made without interfering in any way with the future performance of the tire. (See Fig. 11.) Since the groove is in the form of a segment of a cylinder, its volume can be calculated from its length and its depth at the midpoint.

The reason why great accuracy cannot be obtained with this method is fairly obvious. The method is inherently bad since the rubber has no periods of recovery, such as each little section of a tire tread has after contact with the road surface. With this method the same rubber is in continuous contact with the abrasive wheel, and consequently heat is developed locally and may easily lead to false results. Furthermore, it is imitating a tire on a locked wheel instead of a tire rolling along the road. In general, it may be said that hard mixings are favored by this method.

In an attempt to improve it and to explore its possibilities as a precision machine, this simple tire testing machine was modified by arranging a cam to lift the abrasion wheel off the tire at regular intervals, to simulate the practical conditions of stress and recovery of the rubber. This did not give the desired improvement, however.

(2) A second method is as follows:—A small cylindrical sample about 15 mm. diameter and 3 mm. thick may be extracted from the tire tread in question. The cavity made in the tread may be successfully plugged with a good repair compound, so that the tire may continue its service. This small sample is drilled so that it may be rotated under load, against the periphery of a vertically mounted abrasive wheel.

This wheel is free to rotate about an axis inclined to that of the rubber sample. The arrangement used is shown in Fig. 12. Again the drive and loading arrangements are as previously described, and the machine is similar in principle to that of the Akron Mold Company's machine.

Although the sample in this case is so small, quite reasonable results may be obtained (say within 15 or 20 per cent) provided that the rubber sample will run truly, without vibration. Owing to the fact that the sample is "toed-in" with respect to the abrasive wheel, there is a "lip" formed on one edge, and this aggravates any vibration set up.

This type of machine, with test wheels 4.3 cm. diameter, gives results in good agreement with road performance, provided that the rubber used is within certain limits of hardness. Of course, there is no method of controlling the amount of slip on this machine, other than by altering the angle of the abrasive wheel at the beginning of the test.

Effect of Hardness on Abrasion.—There is no doubt that hardness or rigidity is an important factor in abrasion resistance. It is frequently argued that a soft rubber is distorted more under load than a hard rubber, and therefore, that more slipping or shuffle, resulting in faster wear, occurs with the soft rubber. It does not follow, however, for it has been proved that if two tread compounds have equal tensile strength and equal abrasion resistance (in a laboratory test), then the softer one does not necessarily wear faster than the harder in service. In fact the reverse may be true. In such cases, the softer compound has greater resistance to tearing, for instance.

It is quite certain that there is no straightforward relation between hardness and abrasion in service. As Greider (*Ind. Eng. Chem.*, **15**, 504 (1923)) suggested, the product of rigidity (hardness) and resilient energy is generally a good guide to abrasion resistance, but this rule cannot be applied to all types of compounds. It is a good guide, but abrasion resistance cannot be calculated theoretically with confidence. A check test is always needed.

In the "controllable slip" machine the range of hardness over which correct

relative results may be obtained is greater than that of any other method which has been tried by the writer.

Effect of External Conditions on Wear.—The abrasion resistance of rubber is affected to a marked degree by the external conditions. It has already been mentioned that if a rubber compound is run on a wet abrasive surface, its abrasion is reduced to about one-tenth of its normal value. Of course rubber cuts more readily when wet, but it wears more slowly. This means that tires wear out very slowly when roads are wet.

Temperature also has a decided effect on abrasion. If a set of tires were run at a constantly high temperature, say 90° F., for the whole of their life, they would probably wear out three or four times faster than a set run at a constant 40° F., other conditions being similar. Tires are not treated like that in practice, in England, at any rate, so it is of more practical use to know what variation in wear may be expected from summer to winter for the average tire, which is subjected to the fluctuations of the English climate.

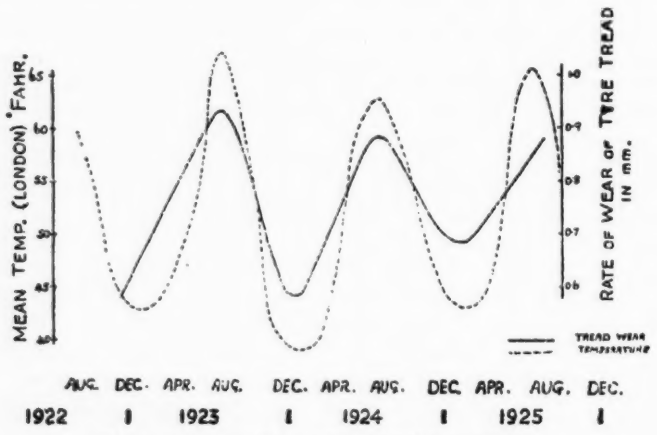


Figure 13—Climatic Conditions and Tread Wear

The rate of wear in the summer may be nearly twice that in the winter, unless the summer is abnormally wet, when the difference is not so marked. This seasonal effect is well illustrated in Fig. 13, which shows the average wear of 736 tires, of the same size and type, running under observation at different periods of the year over a period of three years. This represents an average of about 20 covers per month, each cover running for an average of seven months. The middle month of this period is plotted as abscissa on the graph. Conditions of service vary so much that information of this kind obtained from road tests can only become of value when a large number of covers can be considered.

It will be seen that the peaks on the graph, when the rate of wear was of the order of 0.9 mm. per 1000 miles, occur in the July of each year, while the troughs, when the rate was only 0.6 mm. per 1000 miles, occur in the January of each year.

On the same chart is plotted (see broken line) the mean temperature (London) for the same period, and it will be seen that there is a remarkable agreement between the shape of the two curves. Maximum wear occurs at maximum temperature, and *vice versa*. It is not suggested that the temperature variation is responsible for the variation in wear. It so happens that high temperature and dry weather

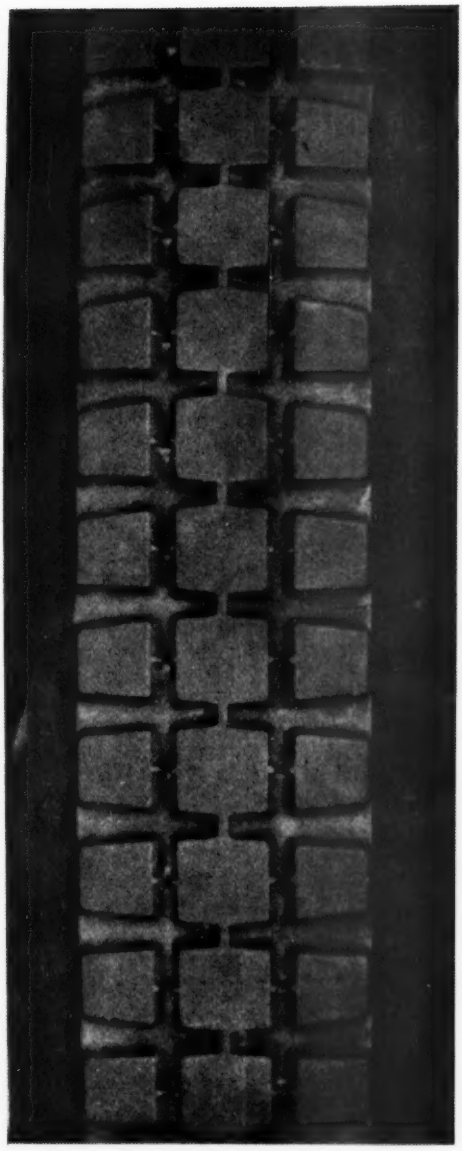


Figure 14—New Tire for Comparison with Figures 15, 19, 20, 21

go together (normally). Moreover, in the summer, the average motorist does more touring over rough road surfaces than in the winter.

As a further illustration of the effect of climatic conditions and of road surface, etc., the following photographs will be of general interest.

Fig. 15 shows two identical tires, run on the same wheel of the same car. The tire on the left ran 8400 miles from December to March, while the tire on the right ran 6000 miles in April, May, and June. The ratio of wear is more than 2 to 1.

Fig. 17 is another example of seasonal wear. The tire on the left ran 10,600 miles

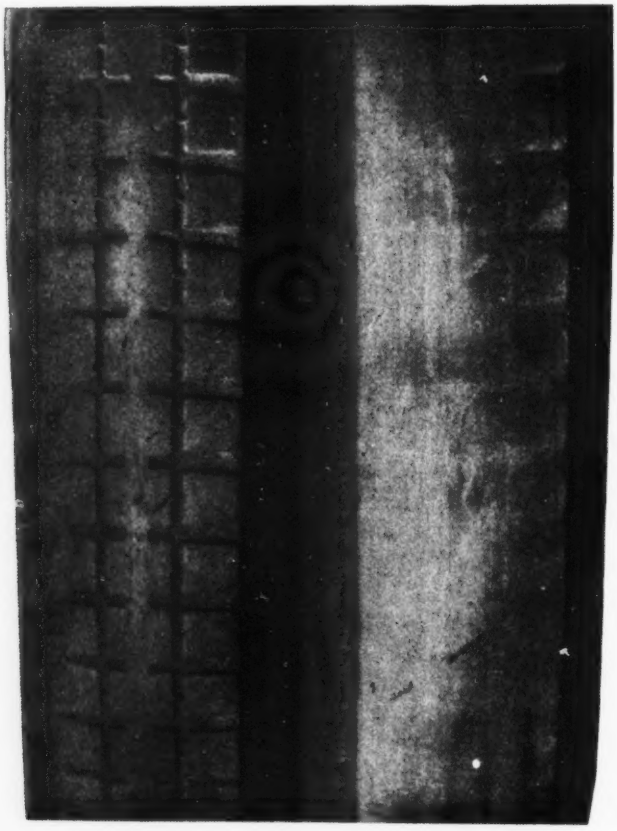


Figure 15

(January to April), while the tire on the right ran 7200 miles (August and September). These are but two examples of many which could be given.

The effect of road surface on tire wear is interesting. The next figure (18) shows an ordinary tarmac road, and Fig. 19 an ordinary waterbound road, of which there are many left in England. Fig. 20 shows, on the right, a tire which ran for the whole of its life on waterbound roads and the rate of wear was at least three times faster than that of the tire on the left, which ran on the ordinary tarmac roads.

As an example of the enormous effects of speed and acceleration on tire wear,

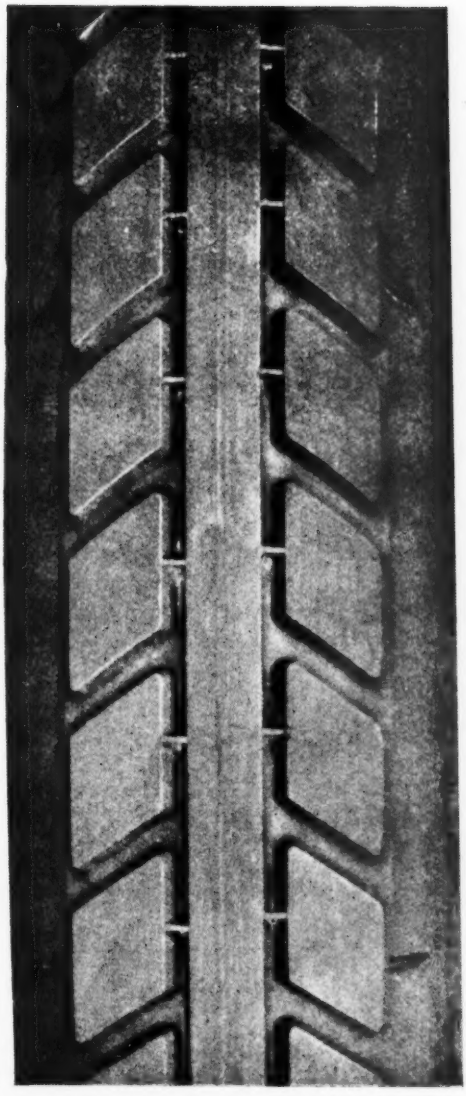


Figure 16—New Tire for Comparison with Figure 17

Fig. 21 is instructive. The tire on the left ran 5000 miles on a touring car under average conditions. The tire on the right did 335 miles on a sports car at an average speed of 90 m. p. h. at Brooklands Racing Track. It will be seen from the photograph that the tires are similar in appearance, and as the ratio of their mileage is of the order of 15 to 1, some idea of the effect of high speed will be obtained. The rate of wear at 120 m. p. h. is approximately 40 times that at 20 m. p. h.

Thus high speed, with the consequent excessive acceleration and braking causes an enormous increase in tire wear. Although the rate of increase of wear from 20

Figure 17

to 40 m. p. h. is lower than that from 40 to 60 m. p. h., it is nevertheless quite marked and will be inevitably reflected in the final mileage of the tire.

It is relevant at this stage to mention the influence of mechanical characteristics of cars on tire wear. Fig. 22 illustrates this. The tire on the left ran 9000 miles on one car, and the tire on the right 3700 miles on another car of the same make and type, in fact identical with the first except that its front wheels had excessive "toe-in." The rate of wear of this tire was nearly five times greater than that of the tire with normal "toe-in."

Needless to say, the above pairs of tires were identical in every respect, otherwise the comparison would be useless.

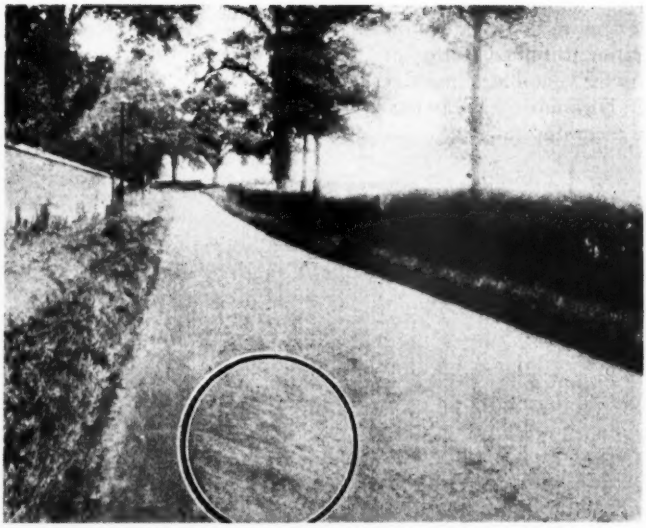


Figure 18

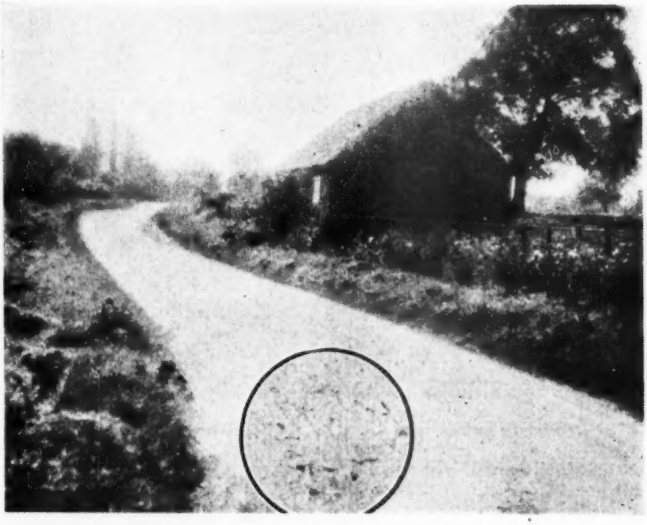
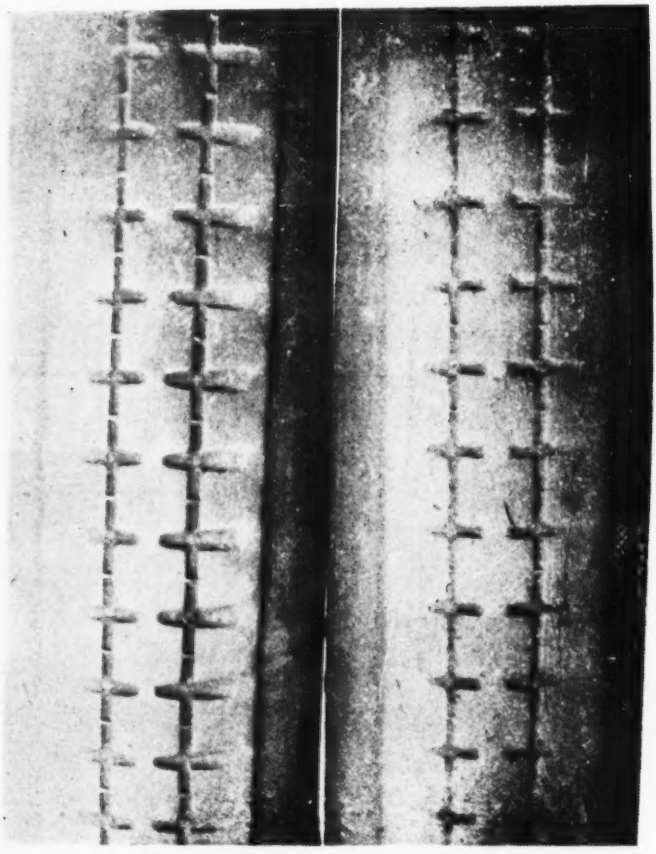


Figure 19

In conclusion, it is to be noted that the variations due to service conditions far exceed those in tire construction; also that the manufacturer has accurate means of testing the abrasion resistance of tread compounds, both before and after the vulcanization of the tire.

Acknowledgments.—The author wishes to express his thanks to Mr. W. H. Paull of the Dunlop Rubber Co., for his permission to publish this paper, to Mr. E. Simpson, for his valuable help in details of construction of the abrasion machine, and to Mr. J. C. Hickman for his assistance with the experimental work and the preparation of the diagrams.



Ordinary tarmac road Waterbound road

Figure 20

Appendix

(*1*) *Calculation of the "Slip."*

Let diameter of abrasive track = D
Let diameter of rubber test wheel = d
Let revolutions of abrasive track = n, in unit time.
Let revolutions of rubber test wheel = N, in unit time.

If there were no slip, the number of revolutions of the track would be given by $\frac{Nd}{D}$

$$\therefore \text{ Slip of track} = \frac{Nd}{D} - n = \frac{Nd - nD}{D}.$$

Expressed as a percentage the slip is $\frac{Nd - nD}{Nd} \times 100 = S$.

The same result is obtained if the slip of the rubber test wheel with regard to the track is taken.

In British units with N equal to 600 and D equal to 6, the calculation is simpler by the first method.

Figure 21

(*2*) *Work Done during Abrasion and Its Relation to Slip.*

Accurate mathematical treatment of the subject of eddy current brakes has been given by W. Rogowski (*Archiv. F. Electrotechnik*, **2,** 205–232 (1912)). Taking the case of a metal plate moving across a magnetic pole with velocity u, it can be shown that the force produced by the reaction of the eddy currents on the field is given by

$$F = ki^2u,$$

where i = current actuating the electromagnet
k = a constant.

Thus, in the "controllable slip" abrasion machine, where the drag is produced by an eddy-current brake, the tractive force is equal to ki^2u. Now:

Total work done on rubber test wheel = work done on rubber test wheel by the driving motor minus work done by the brake

$= ki^2u \times N\pi d - ki^2u \times n\pi D$ (using the notation of paragraph 1)

$$= \frac{ki^2u\pi Nd\ (Nd - nD)}{100\ Nd} \times 100$$

$$= Ki^2uS \text{ where } K = \frac{k\pi Nd}{100}$$

i. e., *the work of abrasion is proportional to the slip.*

(This relation is true for test wheels of a given diameter; in practice, the diameters only vary by about 1 per cent.)

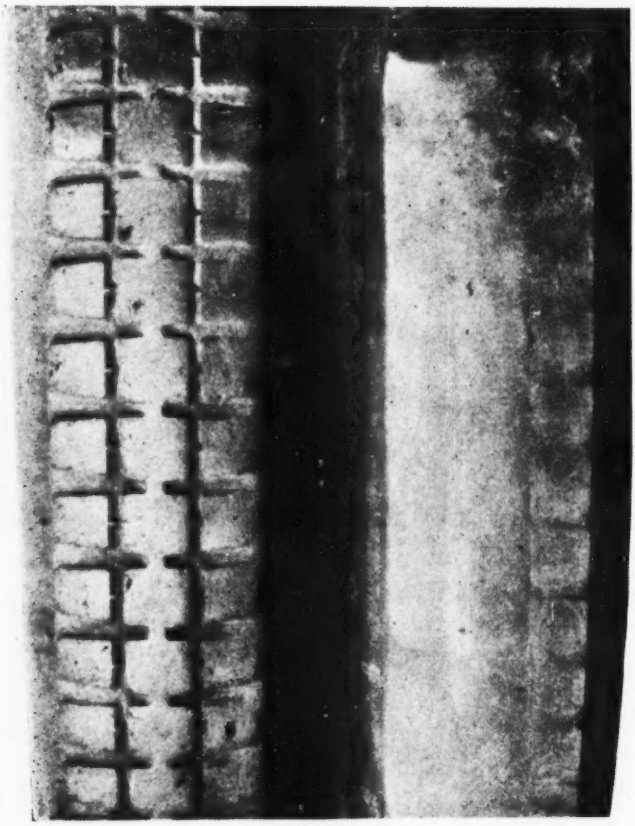


Figure 22

Discussion

The CHAIRMAN said that the controllable slip machine which had been described was attractive. The use of the electromagnetic brake made the control conditions very flexible, and that appeared to be very necessary. It also seemed to have the advantage that it enabled one to control the slip without varying the effects of other factors, such as the hardness, and in that respect the machine had an advantage over the type in which the rubber ran at an angle to the abrasive wheel. He asked Mr. Lambourn if it were

possible to get different relative abrasion values on tires of different tread pattern and, if so, to what extent. Was it possible, for instance, for A's compound to be better than B's compound in A's tire, and for B's compound to be better than A's compound in B's tire? If so, it would appear that it was impossible to speak with as much certainty as we should like to speak of the abrasive resistance of a rubber compound. Those who were concerned with the measurement of abrasion properties would like to express the wearing value of a tire as a product of two figures, one of which expressed the value of the compound and the other the value of the tread pattern. If one could get different relative values according to tread pattern one could not express the value of a tire in that way.

MR. ADAM asked whether there were springs between the abrasive wheel and the tire, because a motor car tire had not a true rolling contact with the road. In the case of a car fitted with a spring, but without shock absorbers, the wheel, when it hit a bump, say, went up six times and came down below the normal center five times, but if shock absorbers were fitted the wheel went up three times and came down below the center twice. In the testing machine, Mr. Lambourn had described, however, the track was quite level.

MR. BARBER asked whether the tires Mr. Lambourn had tested were high or low pressure tires.

MR. FORDYCE JONES said with reference to comparisons between heat and wear he would have liked to have heard more of the effect of different kinds of fillers in the mix. It was to be expected that a tire tread mix loaded with heavy oxides having great heat conductivity might wear more rapidly than a tire loaded with fine non-conduction fillers. The use of fine asbestos powder in this connection might be an interesting subject for experiment.

MR. BIRKITT (Hon. Secretary of the London and District Section), commenting on Mr. Lambourn's reference to the effect of time of cure on abrasion, asked if he had made any variation in the vulcanization of the test samples in order to overcome the difficulties which would arise due to the great difference in thickness of the test piece and the actual tire. Unless some such adjustment had been made, were the results comparable?

DR. SCHIDROWITZ, after expressing his great interest in the paper, said he presumed that if any abrasion occurred at all, that abrasion must correspond to a certain amount of work done. According to Mr. Lambourn the amount of work done was exactly paralleled by slip. Therefore, if there were no slip whatever there would be no work done, there would be no abrasion, and the material would last forever. Possibly the interpretation of the term "slip" would afford the explanation. Also, assuming one had a material which evinced the properties he had mentioned, what would be the general effect, say, on a tire and its movement on the road?

MR. PADDON asked if Mr. Lambourn had made experiments on the abrasion machine to show the effect of varied inflation.

MR. PORTEOUS, commenting on the Chairman's reference to the effect of differences of tread pattern, asked Mr. Lambourn whether a perfectly smooth rubber surface suffered less abrasion than a rough rubber surface. He had in mind a somewhat cognate application, in the case of electric cables with cab tire sheathing used as trailers in coal mines, where they were drawn along behind the coal-cutting machines through the mud and dirt of the mine road. Some users had a very marked preference for a cable sheathing which was perfectly smooth, as against the more easily produced type which had the impression of the cambric tape put over it for the purposes of vulcanization.

MR. MINTON said his personal experience of tire wear was that the back tires of a car always wore out more quickly than the front ones, and if he noticed his front tires wearing badly he wanted to know the reason why—either from the chauffeur or the maker of the car. Mr. Lambourn's scientifically produced results provided much food for thought but, as had already been said, they would have been more complete from a practical point of view if the formulas employed had been given.

MR. LAMBOURN, replying to the discussion, said that tread pattern might influence *relative* abrasion values, probably to the extent of about 10 per cent. The best one could do, as he had said in the paper, was to take the best average relative result and try to get a machine in the laboratory which would give that relative result.

There were no springs between the rubber sample and the abrasive wheel. There was a steady load on the test wheel, and 16 per cent slip was maintained, this figure being chosen because it gave the best average relative results in the great majority of cases, as the figures given in the paper had indicated.

Replying to Mr. Barber, he said that low pressure tires were used in the tests, since the low pressure tire is in vogue today. With regard to the mix he said that even if he were to give the formula of the very best mix he knew of from the abrasion resistance point of view, it did not follow that that mixing would be the best possible from other

points of view, and after all, the tire manufacturer had to consider other things as well as abrasion.

With regard to fillers, he said that zinc oxide certainly had good points so far as high thermal conductivity was concerned, but it was well known that zinc oxide was not the best compounding ingredient from the point of view of abrasion resistance. On the other hand, gas black, which was extraordinarily good from an abrasion resistance point of view, had a nasty habit of causing heat to be developed, and, therefore, in a compound for high speed work the amount of gas black that could be used was limited.

Replying to Mr. Birkitt's question as to the state of cure of the samples tested, as compared with the state of cure of the tires, he said that not only had rate-of-cure tests been carried out on molded samples, but strips had been taken from actual tires, with varying degrees of cure, and tested on the machine, so that he considered the tests were comparable with practical conditions. Replying to the point raised by Dr. Schidrowitz, that if there were no slip there would be no work done on the rubber, and no abrasion, he said he quite agreed, but it must be realized that there must be friction between the tire and the road, otherwise the motor car would not move; if there must be friction there must be work done on the rubber.

Dealing with Mr. Paddon's reference to the effect of varied inflation pressure, he said he had purposely omitted any reference to that, inasmuch as the tire manufacturers had emphasized continually the necessity for checking pressures regularly, and of keeping the tires inflated, but he would take the opportunity of emphasizing the point again. Inflation pressure was an important factor, and a drop of 5 lbs. might easily increase the wear by 20 per cent. Some users allowed the inflation pressure in their tires to drop to half the normal pressure, and they must expect a much greater rate of wear and much less mileage as a result.

Replying to the question put by Mr. Porteous as to whether a smooth surface showed less abrasion than a broken surface, he said he had described in the paper how abrasion depended on the nature of the abrasive surface, the pressure intensity and the amount of slip between the rubber and the abrasive. He said that a perfectly smooth surface would wear at a slower rate than a broken surface since in the former case there was a bigger area and lower pressure intensity. Dealing with Mr. Minton's remarks, he said it was absolutely certain that the back tires would wear out before the front ones a few years ago, before the days of the balloon tire and four-wheel brakes, but nowadays it was quite possible for the front tires to wear away as fast as the back ones. If there were excessive toe-in, the front tires might wear very quickly, and owners of motor cars should pay more attention to the alignment of their front wheels than they did usually. The Rubber Association of America had just issued and was sending out to motor car owners a long pamphlet on the care of tires, impressing upon them the need for looking after their tires with regard to wheel alignment, brake adjustment, etc., because it was possible to wear out a tire five times as quickly as it would wear normally, as the result of excessive toe-in alone.

In connection with the general subject of tread design and the study of tread wear, the reader will be interested in an article by W. L. Holt and C. M. Cook entitled "Measurement of the Tread Movement of Pneumatic Tires and a Discussion of the Probable Relation to Tread Wear," which has appeared in the new publication: Bureau of Standards Journal of Research, Vol. I, No. 1, pages 19–28 (1928). A method and technic is developed for recording graphical impressions of tread movement in general. Copies of this Journal may be obtained from The Superintendent of Documents at Washington upon receipt of twenty-five cents each.—ED.